

Determination of Surface Recombination Velocities of Organic Monolayers on Silicon through Kelvin Probe

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ABSTRACT: We report the determination of surface recombination velocity of electron-hole pairs for silicon samples passivated with organic monolayers by using the Kelvin probe. The recombination velocity was determined by monitoring the surface photovoltage as a function of the incident photon flux. By scanning of the Kelvin probe tip over the sample area, the change in surface recombination velocity can be measured allowing mapping of the recombination

lifetimes. Organic monolayers with different chain lengths and exhibiting various recombination lifetimes were synthesized through a two-step chlorination-alkylation technique. The estimated recombination lifetimes were compared against those obtained from an industrial standard technique using a Sinton WCT-120 and were found to be in good agreement.

INTRODUCTION:

Surface passivation of semiconductor materials is an important factor in the production of high-efficiency devices such as solar cells. In addition to the traditional methods based on inorganic materials, the attachment of organic monolayers has been receiving increased attention in recent years due to the low temperature process of their fabrication (Figure 1).¹⁻⁶ Looking further ahead, organic monolayers may provide a springboard to more ambitious schemes to improve photoexcitation of silicon.⁷

In addition to the intrinsic technological importance, the coverage and recombination lifetime of alkyl monolayers can be changed by changing the alkyl group on the surface, allowing synthesis of samples with a wide range of recombination lifetimes which provide a good research platform for the study of surface recombination.⁸

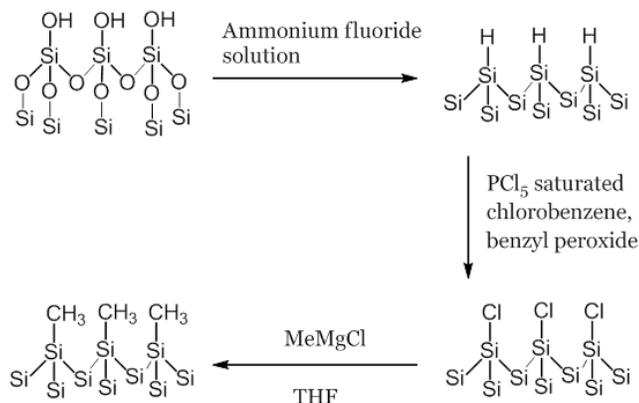


Figure 1. The two-step chlorination-alkylation technique used to produced passivated silicon surfaces

The usual technique for characterizing surface recombination includes microwave reflectance, infra-red absorption, photoluminescence and photoconductance.⁹⁻¹⁴ Among these, the use of transient photoconductance (TPC) methods have become particularly widespread in recent years. Commercially available TPC equipment (such as WCT-120 from Sinton Instruments), in particular, allows the surface recombination lifetime to be inferred speedily and with ease from the total (effective) lifetime including contributions from both surface and the bulk.

This paper develops a novel procedure which allows the determination of the surface recombination velocity by using the Kelvin probe. The Kelvin probe is a powerful and versatile tool for characterizing metal and semiconductor surfaces by measuring the work function.^{15,16} This allows the determination of a variety of electronic parameters pertaining to the surface but also the bulk. In application to semiconductors, it provides a particularly useful tool to measure the surface potential barrier (band bending) by monitoring the surface photovoltage: the illumination-induced changes of surface electrostatic.¹⁷⁻²⁰ We extend this effectively static picture by homing in on the surface photocurrent, to determine the surface recombination velocity. We also show that the method can be developed into a scanning technique which images with ease the recombination lifetime of an entire wafer.

MATERIALS AND METHODS

The silicon samples (n-type, 111, FZ, $25 \Omega \text{ cm}^{-1}$, $525 \mu\text{m}$ thick from Siltronic) used in this paper were synthesized as per our previous paper,²¹ using a two-step chlorination-alkylation technique that has been shown to impart passivation. To provide control samples with high

surface recombination velocity we synthesized samples where the surface was intentionally contaminated with palladium, by immersing an allyl passivated sample in a solution of palladium acetate (0.1 g) in THF (10 mL) for 10 minutes.

Kelvin probe measurements were performed on a scanning Kelvin Probe system (SKP5050) from KP Technology, fitted with an X-Y-Z sample holder. To achieve a good contact between the wafer and sample stage, the rear side of the wafer was scratched with sand paper to remove any insulating oxide, and applying silver paste. After placing the wafer on the sample stage, the paste was allowed to dry for 24 hours prior to measurements.

Samples were illuminated by optical fiber with a xenon lamp source. To achieve different values of photon flux, a variable slit was used in the optical fiber. The photon flux was estimated using a calibrated photodiode under the same conditions as the illuminated samples.

The proposed method for the determination of the surface recombination velocity from the surface photovoltage relies on analyzing the current balance near the surface (Figure 2).

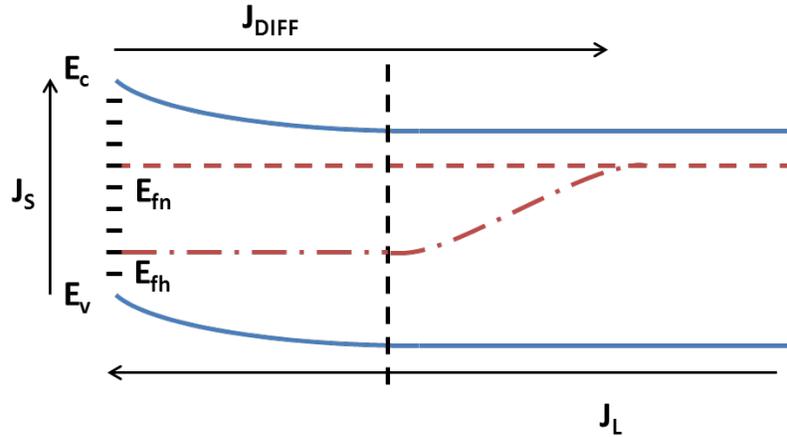


Figure 2. The surface bands for an n-type silicon wafer (not to scale) showing the quasi-Fermi levels for electrons and holes (E_{fn} and E_{fh}), the photogenerated current for minority carriers (J_L), the surface recombination current (J_S) and the diffusion current J_{DIFF} resulting from carrier injection due to surface photovoltage and quasi-Fermi level splitting near the surface.

Electron-hole pairs are generated in the bulk, where they diffuse towards the surface giving rise to the photogenerated current J_L . Denoting the probability that they reach the surface (i.e., the collection efficiency) by η_c , J_L is given by:

$$J_L = q\phi_0(1 - R)\eta_c \quad (1)$$

where ϕ_0 is the incident photon flux, R is the surface reflectivity and q is the electron charge. As the diffusion length for the samples was twice as large as the wafer thickness it is safe to assume that all minority carriers generated in the bulk reach the surface, and equate the collection efficiency to unity.

The net surface recombination current J_s is proportional to the difference between the recombination rate and the (thermal) generation rate, i.e., to the difference

$$(p_s n_s - p_0 n_0) \quad (2)$$

where p_s and n_s are the surface electron and hole concentrations, and p_0 and n_0 are the concentration of electron and holes in equilibrium. Using the mass action law, and introducing the surface photovoltage V we can therefore write

$$J_s = J_{0s} \left(\frac{n_s p_s}{n_i^2} - 1 \right) = J_{0s} \left(e^{\frac{qV}{k_B T}} - 1 \right) \quad (3)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and J_{0s} is a constant which can be linked to the surface recombination velocity S as follows. Since our samples operate under weak injection throughout (including the surface), the electron (majority carrier) concentration remains unchanged by illumination, the surface recombination current can be written in terms of the surface recombination velocity as

$$J_s = qS(p_s - p_0) \quad (4)$$

Equating (3) and (4) then gives

$$J_{0s} = qSp_0 \quad (5)$$

Collecting all terms we obtain

$$(J_{0s} + J_0) \left(e^{\frac{qV}{kT}} - 1 \right) = \Phi_0(1 - R) \quad (6)$$

where qV is given by the splitting of the quasi-Fermi-levels as shown in figure 2.

The constant J_0 corresponds to the usual dark saturation current in the Shockley diode equation, and can be estimated accordingly by the expression²²

$$J_0 = qp_0 \sqrt{\frac{D}{\tau_b}} \quad (7)$$

Using the parameters for our wafers yields an upper bound on J_0 of 5×10^{-14} A cm⁻². This is three orders of magnitude smaller than the values we obtain for J_{0s} , indicating that recombination is dominating at the surface and J_0 in Eq. (6) can be neglected.

By virtue of the long bulk lifetime guaranteed (in excess of 1000 μ s as checked also by control measurements of samples under study after the surface treatment) the surface recombination velocity by Kelvin probe was converted to surface recombination lifetime by:

$$\tau_s = \frac{W}{2S} \quad (8)$$

Illumination by a xenon lamp generates carriers mostly close to the surface (within approximately 10 μ m) which allows the diffusion limited component of surface recombination lifetime to be neglected.

The I-V type dependence of the current density on the surface photovoltage has previously been investigated by Watanabe et al.²³, where it was shown that two regions exist in the curve. At low illumination intensities, the I-V type dependence is non-linear and is not currently well understood. At larger illumination intensities the I-V type characteristic is shown to be linear over a wide range and is proportional to the surface recombination current. This is the area investigated in this paper and is shown in Figure 3.

RESULTS AND DISCUSSION: 1D APPLICATION

By variation of the photon flux, and recording of the quasi-Fermi-level splitting through the use of a Kelvin probe, the value of J_{0S} can be determined. A graph of $(e^{qV/kT}-1)$ against $\phi_0(1-R)$ therefore yields J_{0S} as the gradient. The gradient for various different recombination lifetime samples synthesized and the corresponding lifetime as measured by the Sinton WCT-120 are shown in Figure 3.

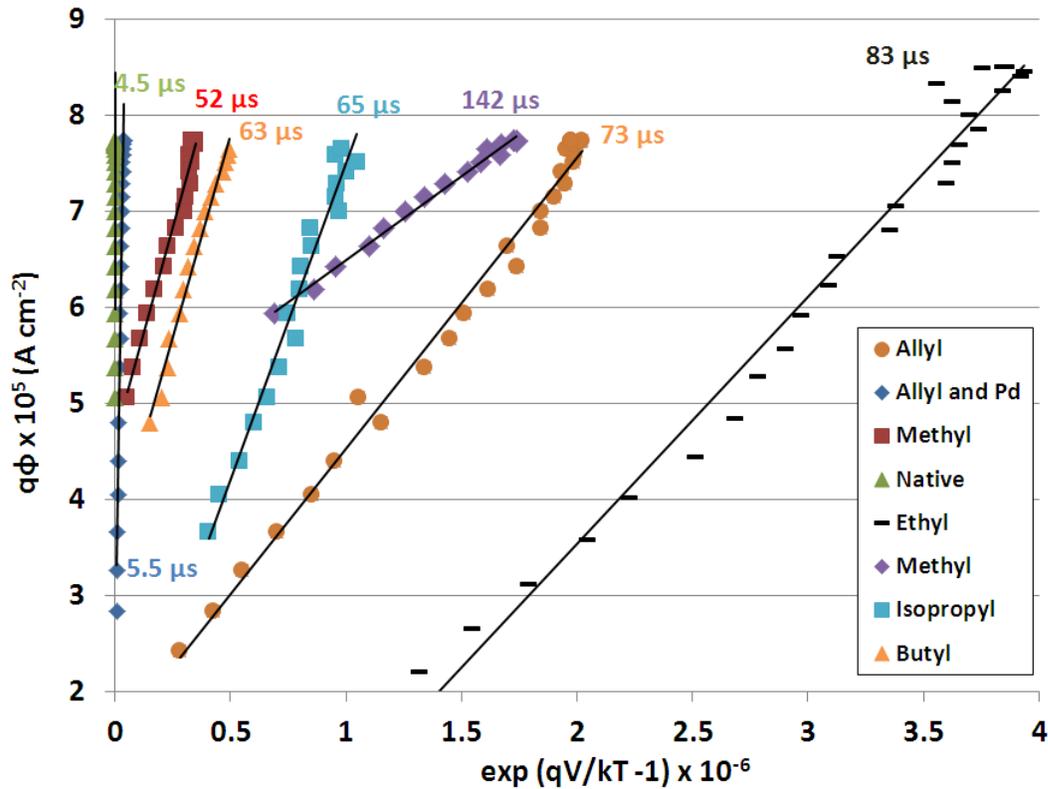


Figure 3. Graph showing the I-V type relationship for various differently passivation samples as measured by the Kelvin probe with the recombination lifetime as measured by the Sinton WCT-120. The inverse relationship between the slope of the graphs and surface lifetime can be clearly visible, and is quantified in Table 1

A good agreement is observed between the recombination lifetime values calculated from the Kelvin probe data and the Sinton lifetime tester, with higher lifetimes measured by the Sinton

leading to a higher calculated value by the Kelvin probe (Table 1). The difference between the two is likely to be a combination of experimental error and due to the Sinton giving an average lifetime value, which takes into account the full sample area. The Kelvin probe method looks at a smaller area and is therefore this is more sensitive to small changes in the passivation layer, which can affect the recombination lifetime. This is useful as it allows us to map the lifetime changes over the sample area by moving the X-Y stage.

Sample	Sinton WCT-120			Kelvin Probe		
	Measured Lifetime (μs)	Implied S (cm s^{-1})	J_{0S} (A cm^{-2})	Measured S (cm s^{-1})	Measured Lifetime Implied (μs)	
Native	4.5	Very High to (1×10^5 to 1×10^7)	5.47×10^{-7}	5.83×10^6	0.004	
Methyl	142	185	1.74×10^{-11}	162	154	
Ethyl	83	316	2.57×10^{-11}	239	104	
Butyl	63	417	8.37×10^{-11}	776	32	
Isopropyl	65	404	6.45×10^{-11}	601	42	
Allyl	73	359	3.31×10^{-11}	308	81	
Allyl / Pd	5.5	Very High to (1×10^5 to 1×10^7)	1.96×10^{-9}	1.83×10^5	0.137	

Table 1. A summary of the different passivated sample with the recombination lifetime and implied surface recombination velocity as measured by the Sinton WCT-120 and the Kelvin probe

The change in recombination with different surface termination is due to the surface coverage, and has been explored in detail by Lewis *et Al.*² They found that methyl-terminated surfaces have a higher surface coverage (and recombination lifetime) than other straight-chain alkyl groups due to their small size. Bulkier groups such as tertiary-butyl and iso-propyl have a lower surface coverage due to steric hindrance, and thus have the lowest recombination lifetime. This gives us a wide variety of different recombination lifetime samples to test with our technique.

To further confirm the technique was correctly monitoring the surface recombination velocity, the recombination lifetime of a highly-passivated (allyl-terminated) surface was reduced whilst on the rig using palladium. The value of J_{OS} , and thus the value of recombination lifetime, decreased immediately, confirming that the difference in J_{OS} was due to the different sample lifetimes.

In Figure 4, the correlation between the surface recombination velocity as measured by the Kelvin probe and Sinton WCT-120 method is shown. A linear trend would correspond to equal values obtained by the two measurement techniques and is marked with a dashed line. It is seen that the results for surface recombination velocity are similar, within experimental errors which are discussed below.

The Sinton WCT-120 measures the average lifetime over the sample, such that low-lifetime areas such as the edges (due to saw-damage) are included in the measured lifetime. For the Kelvin probe technique, the data is obtained in the surface-probe tip interaction area, which is around 1 mm^2 . Therefore this is less sensitive to the low-lifetime areas, resulting in the difference in SRV between the two techniques.

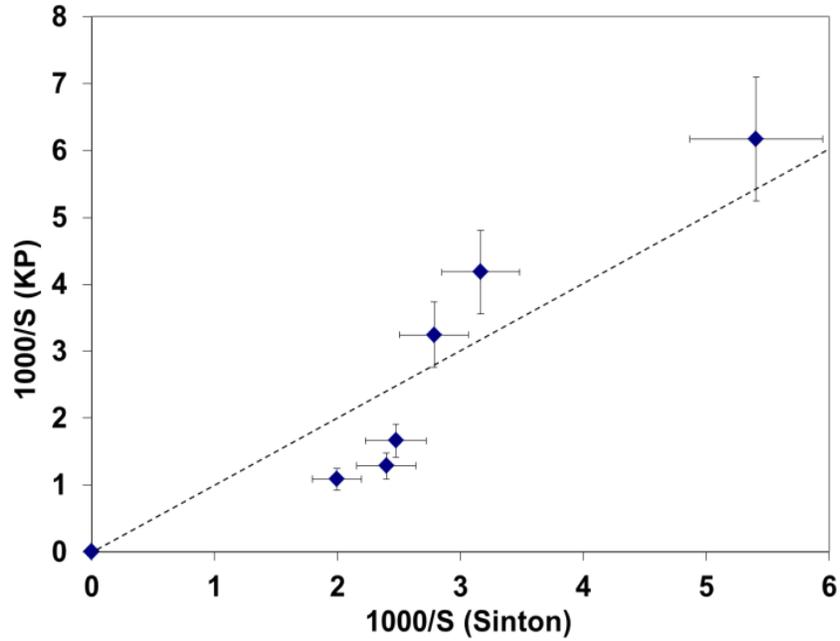


Figure 4. The surface recombination velocity as measured by the Kelvin probe against that measured by the Sinton WCT-120. The dashed line indicates the expected linearity.

2D APPLICATION

The new technique for measuring recombination lifetime could be used to map sample lifetime over a large area such as a complete wafer. This mapping technique can be easily automated by using two points on the linear part of the graph (at photon fluxes of 3.86×10^{14} and 4.77×10^{14} photons $\text{s}^{-1} \text{cm}^{-1}$), with the gradient calculated between these values. This was repeated for the entire sample, giving the change in surface recombination velocity (and therefore recombination lifetime) over the whole sample. The surface recombination velocity maps and their corresponding lifetime maps (as calculated from equation 8) are shown for a methyl- and ethyl-terminated surface are shown below.

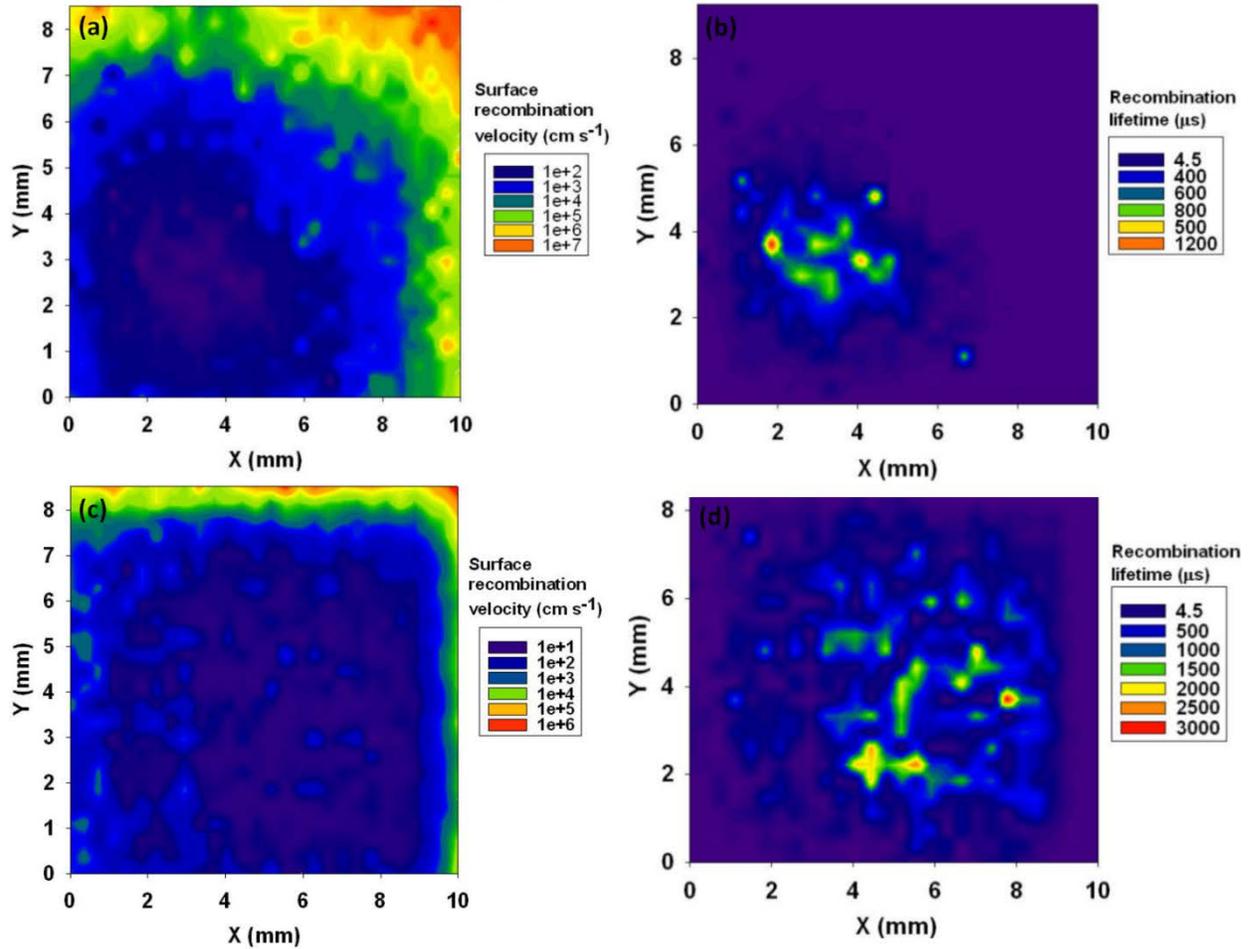


Figure 5. The surface recombination velocity map of a methyl- (a) and ethyl-terminated (c) surface with the corresponding recombination lifetime maps (methyl (b) and ethyl (d))

The edges of the passivated samples appear to have a reduced surface recombination velocity when compared to the center. This is not surprising, as the edges have a higher area for recombination than the center, as well as saw damage from wafer dicing, similar to other literature findings.

The native oxide samples showed a low lifetime throughout the sample, with the majority of the sample showing a lifetime of less than 20 μs . Several higher lifetime areas ($<50 \mu\text{s}$) are visible, which could be due to some surface contamination.

The high lifetime (142 μs) methyl terminated surface contained an area of low recombination in the lower left corner (Figure 5b). Compared to that of the ethyl terminated surface (Figure 5d), this area contains a more uniformly high lifetime section. Although containing areas with a higher maximum recombination lifetime, the ethyl-terminated surface exhibits a lower overall lifetime (83 μs) as measured by the Sinton WCT-120. This is likely due to the ‘patchy’ nature of the passivation in the high lifetime areas; the high lifetime sections are intersected by very low lifetime areas, which allow for fast recombination rates. Therefore the flow of electrons from the high lifetime areas to the low will be fast, as minimal distance (and less diffusion) is required to reach the recombination centers. In the methyl surface however, large areas of the surface are well passivated, meaning that the minority carriers need to flow for a large distance before they reach recombination centers. This allows for a long recombination lifetime, and thus a low surface recombination velocity. We have also tested this technique with great success on amorphous silicon passivated surfaces.

It should be noted that the new mapping technique for the recombination lifetime of wafers may find a ready application in industry as there are very few techniques available to do this task (infrared lifetime mapping,^{10, 11, 24} microwave reflectance⁹ and photoluminescence imaging¹²), making this a valuable technique in the determination of passivation quality.

CONCLUSIONS

A novel technique has been developed to measure the surface recombination velocity and recombination lifetime of silicon samples. By changing the incident photon flux on the sample in a Kelvin probe, the photogenerated current can be calculated and the change in surface photovoltage measured. This allows the surface dark current (J_{0S}) to be extracted, from which

the surface recombination velocity and recombination lifetime can be calculated. The results fit closely with those of the Sinton WCT-120, confirming the theory.

By applying the same principal to a 2D scan of the wafer, the surface recombination velocity and recombination lifetime can be plotted over the sample area, allowing defects in the surface passivation to be investigated. Few techniques are currently available that can map wafer lifetimes (infrared lifetime mapping, microwave reflectance and photoluminescence imaging) making this technique valuable in semiconductor quality analysis.

Thus the Kelvin probe has been shown to be a very sensitive technique for surface analysis, and an attractive method at characterizing the passivation of semiconductor surfaces.

SUPPORTING INFORMATION

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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