Electronic Properties of Si Surfaces and Side Reactions during Electrochemical Grafting of Phenyl Layers

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The electrochemical grafting process of 4-nitrobenzene and 4-methoxybenzene (anisole) from diazonium salt solutions has been investigated in situ by monitoring the current density, the band bending, and the nonradiative surface recombination during grafting at different potentials and different concentrations of the diazonium salt in the solution. Ex situ infrared spectroscopic ellipsometry has been used to inspect the Si surface species before and after the grafting process. The band bending decreases with either increasing concentration of diazonium salt or when the redox potential of the diazonium compound (anisole) is nearer to the competing H^+/H_2 couple. The surface recombination increases at more cathodic potentials if an electron donor group is present at the phenyl ring (nitrobenzene) and vice versa for the electron acceptor group (anisole). The influence of side reactions can be reduced by use of moderate concentration and moderate or strong cathodic potential, depending on the redox potential of the diazonium compound.

Introduction

The preparation and characterization of silicon (Si)/organic layer interfaces is of great importance for future applications in sensors, new devices, or for living cell immobilization at semiconductor (i.e., Si) surfaces.[1−7] Electronic devices need chemical and electronic passivation of the Si/organic layer interfaces, which have to be performed at low thermal budgets to ensure nondestructive processing. Additionally, the traditional postannealing of Si/SiO_2 interfaces in forming gas above 400 °C is no longer valid. Therefore, the passivation and functionalization of the Si/organic layer interface must be obtained simultaneously with the grafting process.[4,8] Electrochemical grafting seems to be a very promising method to produce well passivated Si/organic layer interfaces, even in the submonolayer regime.[4,9−13]

A method to graft phenyl layers from the respective diazonium compounds on Si(111) surfaces has been proposed by Allongue et al.[10] Cathodic reduction of diazonium salts in aqueous solution is of interest for devising a simple grafting technique in aqueous solution at negative potentials. Hartig et al.[4] developed a well-reproducible grafting technique by applying an injection method without any HF present in the electrolyte.

However, the mechanism of the deposition process is not completely understood yet because of its complexity. One reason for such complex mechanism is a formation of intermediate radical species, which have typically high oxidation power. In this article, we study the effect of change of the dipole moment orientation of the intermediate species on the reaction mechanism.

There is no change in dipole orientation after transition of 4-nitrobenzenediazonium tetrafluoroborate (4-NBDT) to the 4-nitrobenzene radical, but a huge change in the case of the 4-methoxybenzenediazonium tetrafluoroborate (4-MeBDT) transition to 4-methoxybenzene radical.[8] This behavior should result in significant differences in surface chemical reactions where phenyl ring grafting competes with side reactions (dimerization, reaction with the solvent or other diazonium molecules).

The objective of the present paper is to determine the effect of the redox potential of diazonium compounds, the electron transfer via the conduction band of p-Si, and radical-induced side reactions on the grafting process. Therefore, the amount of Si-phenyl, Si−OH, SiO_x, and Si−H surface species should differ.

We used in situ pulsed photoluminescence (PL) and pulsed photovoltage (PV)[14] techniques to inspect the nonradiative recombination and band bending during the grafting process.[15,16] The measured PV (U_{PV}) is sensitive to surface potential variations induced by organic surface molecules when the latter reach densities on the order of 10^{14} cm^{-2}. The PL intensity (I_{PL}) is sensitive to very low concentrations of surface recombination centers (on the order of 10^{10} cm^{-2}) and is proportional to the reciprocal of the defect concentration.[15]

Additionally, we applied ex situ infrared spectroscopic ellipsometry (IRSE) to inspect the amount of SiO_x and Si−H on the Si surface[17,18] before and after the grafting process.

Experimental Section

Wafers of p-Si(111) (2.5−5 Ωcm) were cleaned by using a standard procedure and thermally oxidized (the thermal oxide

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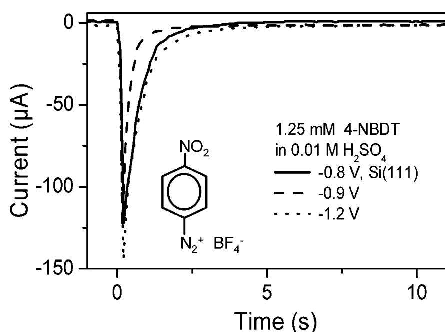


Figure 1. Current transients during electrochemical grafting of 4-NB onto hydrogenated Si(111) at different negative potentials. Time scale has been set to zero when the diazonium salt was added to the solution. The simplified structure of the 4-NBDT molecule is sketched as an insert.

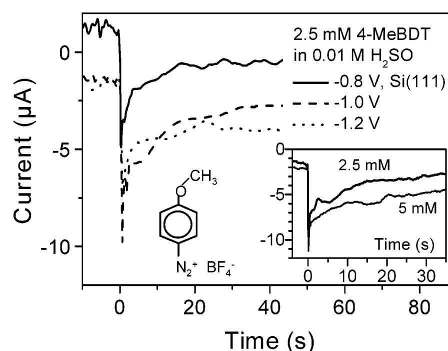


Figure 2. Current transients during electrochemical grafting of 4-MeB onto hydrogenated Si(111) at different negative potentials and different concentrations of 4-MeBDT (see insert). Time scale has been set to zero when the diazonium salt was added to the solution. The simplified structure of the 4-MeBDT molecule is sketched as an insert.

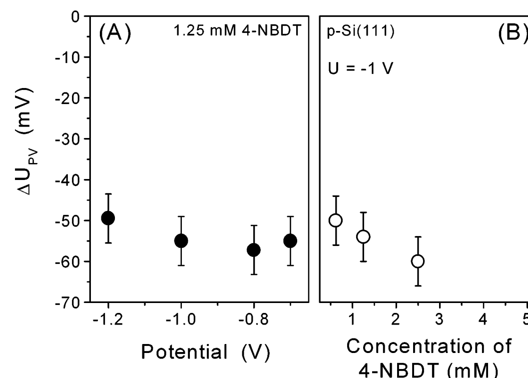


Figure 3. Change in band bending (ΔU_{PV}) after grafting of 4-NB on Si(111) as a function of (A) the applied potential using a 1.25 mM 4-NBDT solution and (B) the concentration of 4-NBDT at −1 V in 0.01 M H_2SO_4.

thickness was about 100 nm). The wafers were cut into 20 × 20 mm^2 samples. The samples were ultrasonically cleaned in acetone and water, and then the thermal oxide was etched in 2% HF, and a chemical oxide was formed in H_2SO_4/H_2O_2 = 1:1 solution for 10 min. The back contact was made by depositing InGa eutectic after the chemical oxide had been etched by using a droplet of 2% HF. The front surface of the sample was not affected by the preparation of the back contact. The electrochemical preparation of the front surface was performed in a single-compartment Teflon cell, using a three-electrode configuration (sample−working electrode, Au ring−counter electrode, Au wire−reference electrode). The sample was mounted into the cell and the chemical oxide was etched back in NH_4F (40%), such that flat hydrogenated Si(111) terraces were formed.[19] The NH_4F (40%) was then completely pumped out, and the cell was filled with 20 mL of 0.01 M H_2SO_4. Simultaneously, the potential was switched to −1.4 V vs the Au reference electrode to ensure that the H-terminated Si surface was not oxidized. Then, the potential was switched to the desired value. Afterward, 10 mL of the supporting electrolyte was pumped out and 10 mL of the diazonium salt solution (4-NBDT or 4-MeBDT) in 0.01 M H_2SO_4 was injected into the cell at constant potential. Thus, electrochemical grafting of 4-nitrobenzene (4-NB) or 4-methoxybenzene (4-MeB) molecules, respectively, occurred.

Time-resolved PV (time resolution 20 ns) and time-integrated PL signals (integration time 100 μs) were excited by single pulses of a nitrogen laser pumped dye laser (wavelength 500 nm, duration time 10 ns, intensity 40 μJ cm^{-2}). The in situ PV and PL measurement procedures were described in detail in ref 16.

The IRSE measurements were performed by using a photometric ellipsometer,[20] which was attached to a Bruker IFS 55 Fourier transform spectrometer or to the infrared beamline at BESSY II.[21] The ellipsometric parameters are derived from the ratio of intensities of single-beam spectra measured for four different polarizer positions (0°, 45°, 90°, 135°). A second set of measurements performed with a KRS5 retarder provides for the accurate determination of Δ for values of |cos Δ| ∼ 1. A liquid nitrogen-cooled mercury cadmium telluride (MCT) detector was used in all measurements.

Results

(a) Current Transients during Diazonium Salt Injection. Figures 1 and 2 show the time dependence of the current during electrochemical grafting of 4-nitrobenzene (4-NB) and 4-methoxybenzene (4-MeB) on hydrogenated Si(111) at different negative potentials. The time scale had been set to zero when the diazonium salt was added to the solution. The current density increases immediately after the addition of the diazonium salt solution due to the electron transfer from the working electrode to the diazonium ions in solution (initial current). The initial current for grafting of 4-NB (Figure 1) is much higher than for 4-MeB (Figure 2). The time until the current transient has decayed (final current) is about 10 times faster for the grafting of 4-NB than for 4-MeB. However, the final current approaches its value, which it had before the addition of the diazonium salt, more closely for 4-NB on Si than for 4-MeB on Si. The final current reaches more negative values at −1.2 V than at −1 or −0.8 V, respectively. The inset in Figure 2 shows the concentration dependence of the current kinetics for the grafting of 4-MeB at −1 V in 0.01 M H_2SO_4. The final current is more negative than before the grafting process. The increase in concentration of 4-MeBDT has a similar effect on the final current as an increased cathodic potential (see Figure 2). The anodic current just before the addition of the diazonium compound at a potential of −0.8 V indicates an oxidation of the Si surface (see Figure 2).

(b) Photovoltage Variations. Figures 3 and 4 show the change in band bending (ΔU_{PV}) (relative to its value for H-terminated surfaces) as a function of the applied potential at a fixed concentration of the diazonium salt (A) and as a function of the concentration at constant potential (B) after grafting of 4-NB (Figure 3) and 4-MeB (Figure 4) on Si(111) from 4-NBDT and 4-MeBDT solutions, respectively. The change in band bending is about −58 mV (reduction of band bending due to negative surface charge for p-type Si) and quite independent of

the applied potential and the concentration for grafting of 4-NB (Figure 3), whereas the ΔU_{PV} increases from −10 to about −40 mV for the grafting of 4-MeB with increasing negative potential or concentration of 4-MeBDT (Figure 4).

ΔU_{PV} has been measured after about 20 s of grafting. Thereafter, the measured value does not change significantly, as opposed to the behavior of the PL with time. In this case, ΔU_{PV} is saturated, while the PL still rises because it is more sensitive to dangling bond densities ranging from 10^{12} to 10^{10} cm^{-2}.[4,8]

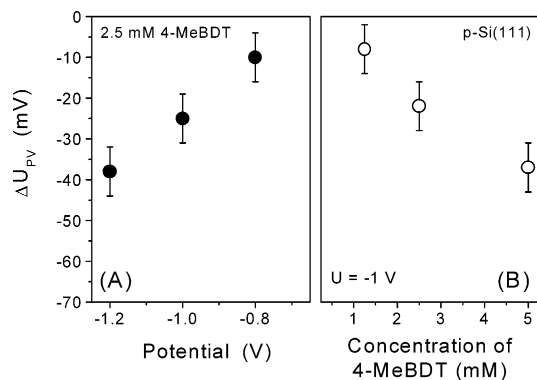


Figure 4. Change in band bending (ΔU_{PV}) after grafting of 4-MeB on Si(111) as a function of (A) the applied potential using a 2.5 mM 4-MeBDT solution and (B) the concentration of 4-MeBDT at −1 V in 0.01 M H_2SO_4.

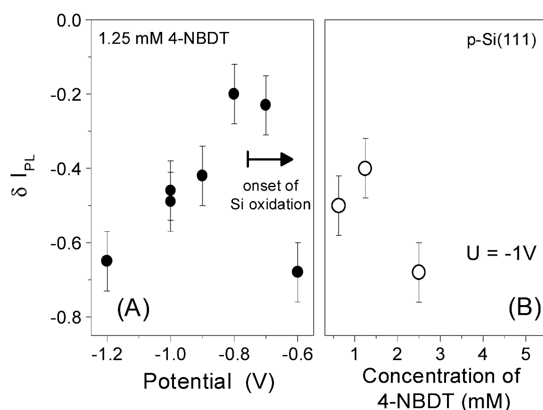


Figure 5. Relative change of PL intensity (δI_{PL}) after about 2000 s of grafting of 4-NB onto Si(111) as a function of (A) potential and (B) concentration of the 4-NBDT salt, respectively.

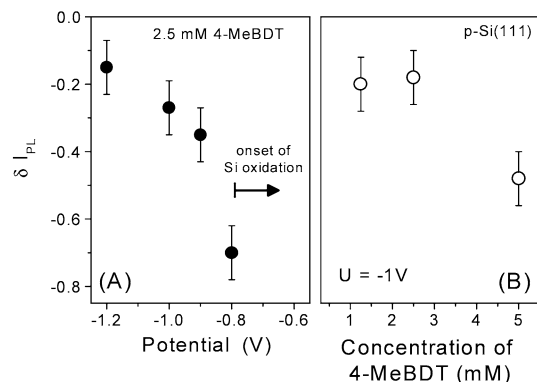


Figure 6. Relative change of PL intensity (δI_{PL}) after about 2000 s of grafting of 4-MeB onto Si(111) as a function of (A) potential and (B) concentration of the 4-MeBDT salt, respectively.

(c) Surface Recombination. Figures 5 (for 4-NB) and 6 (for 4-MeB) show the relative reduction of the PL intensity (δI_{PL} = $[I_{PL}(2000\ s) - I_{PL}(0\ s)]/I_{PL}(0\ s)$), with respect to the H-terminated surface at the same potential, after about 2000 s of grafting as a function of the applied potential (A) and of the diazonium salt concentration (B). The time of about 2000 s is required for PL measurements due to the fact that I_{PL} is sensitive to dangling bond densities ranging from 10^{12} to 10^{10} cm^{-2} and the radical reactions at the Si surface need this time to passivate Si dangling bonds with respect to an increased steric hindrance at the phenyl-covered Si surface. The coverage of phenyl groups on Si(111) surfaces is known to be about 50%. δI_{PL} decreases to about −0.65 (i.e., the amount of nonradiative recombination active centers is enlarged by about 65%) at a potential of −1.2 V during the grafting of 4-NB (Figure 5A). The decrease in δI_{PL} is less pronounced at −0.8 V, i.e., the Si surface is better passivated at −0.8 than at −1.2 V. The values at −0.7 and −0.6 V in Figure 5A and at −0.8 V in Figure 6A reflect the onset of the competing anodic oxidation of the Si surface in aqueous solution at such potentials, which leads to defect formation and, consequently, to the quenching of I_{PL} and to an increase of δI_{PL}. The oxidation of the Si surface is reflected by an anodic current before the grafting process, which is well resolved in Figure 2 (−0.8 V at times <0 s).

The behavior of δI_{PL} as a function of the applied potential is completely different for the grafting of 4-MeB (Figure 6A) in comparison with 4-NB (Figure 5A). However, the dependence of δI_{PL} on the diazonium salt concentration at fixed potential (here −1 V) is similar for both diazonium salts: δI_{PL} increases in more concentrated solutions (see Figures 5B and 6B).

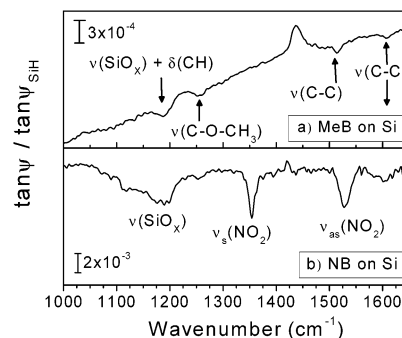


Figure 7. Relative change of IRSE (tan Ψ/tan Ψ_{SiH}) spectra for 4-MeB (a, top) and 4-NB (b, bottom) grafted onto p-Si(111) surfaces.

(d) Infrared Spectroscopic Ellipsometry. The relative change in the IRSE spectra (tan Ψ/tan Ψ_{SiH}) for 4-NB and 4-MeB grafted on Si(111)/H surfaces are plotted in Figure 7. Highly doped p^+-Si(111) was used for the grafting of 4-MeB to reduce the influence of IR reflection from the backside during the measurement. The weak IR absorption at about 1250 cm^{-1} is due to the C−O−CH_3 stretching vibration.[22] However, some NH_4^+ ions are still present at the surface of the highly doped p^+-Si, as can be seen by the absorption signal at about 1450 cm^{-1}.[23,24] The IR absorption due to symmetric and asymmetric stretching modes of the NO_2-group (around 1350 and 1530 cm^{-1}) and some ring vibrations at about 1620 cm^{-1} are well seen.[25] Additionally, there is an IR band at about 1130 cm^{-1}, which is a result of SiO_x stretching vibrations. The behavior of this IR absorption will be investigated in more detail in the next paragraphs.

The grafting of 4-NB on Si leads to the formation of SiO_x surface species independent of the applied cathodic potential (Figure 8A). The amount of SiO_x seems to be unchanged with increasing cathodic potential. The sharp absorption due to Si−H surface bonds on a flat Si(111)/H surface is well seen before the electrochemical treatment (Figure 8B), whereas no Si−H

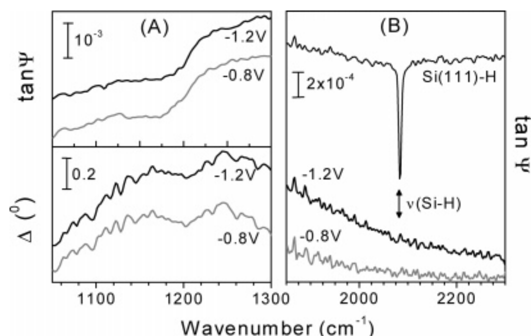


Figure 8. IRSE spectra for 4-NB grafted onto p-Si(111) surfaces at different potentials: (A) tan Ψ and Δ spectra in the SiO_x vibrational range and (B) the tan Ψ spectra in the Si−H vibrational range. The absorption signal due to Si−H stretching mode of a flat and H-terminated Si(111) surface before the grafting process is plotted in B.

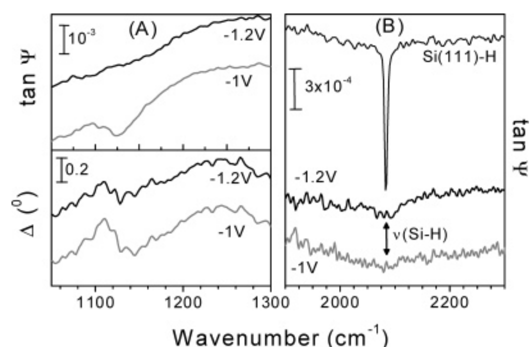


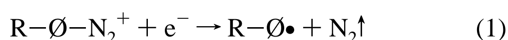
Figure 9. IRSE spectra for 4-MeB grafted onto p-Si(111) surfaces at different potentials: (A) tan Ψ and Δ spectra in the SiO_x vibrational range and (B) the tan Ψ spectra in the Si−H vibrational range. The absorption signal due to Si−H stretching mode of a flat and H-terminated Si(111) surface before the grafting process is plotted in B.

surface species could be detected after the grafting process (Figure 8B) at −1 and −1.2 V, respectively.

This behavior is different for the grafting of 4-MeB onto Si(111) surfaces from the 4-MeBDT salt. The amount of SiO_x decreases strongly at higher cathodic potentials (Figure 9A), leading to an almost oxide-free surface. Small amounts of Si−H are still present after the grafting process and seem to increase from −1 to −1.2 V (Figure 9B).

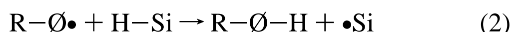
Discussion

(a) Grafting and Some Possible Side Reactions in Aqueous Solution. In the following, we will discuss some possible side reactions that compete with the main process, the grafting of diazonium radicals at the Si surface. The first step of the electrochemical grafting of organic layers from diazonium compounds is the electron transfer to the diazonium ion (see eq 1, Ø denotes the phenyl ring). The electron transfer is not the rate-limiting step and is electrostatically favorable because the diazo (N_2^+) group is positively charged, while the Si surface is negatively polarized.[10]



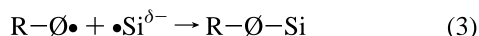
$$R{-}Ø{-}N_2^+ + e^- \rightarrow R{-}Ø\bullet + N_2\uparrow \quad (1)$$

Reaction 2 is mainly responsible for Si surface dangling bond formation and reaction 3 is



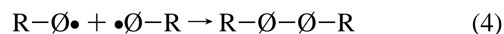
$$R{-}Ø\bullet + H{-}Si \rightarrow R{-}Ø{-}H + \bullet Si \quad (2)$$

finally, the bonding of a phenyl ring onto the Si surface.



$$R{-}Ø\bullet + \bullet Si^{\delta-} \rightarrow R{-}Ø{-}Si \quad (3)$$

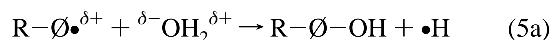
Furthermore, reaction 4 describes the dimerization of two phenyl rings, so that this reactive radical species is no longer available for the grafting process.



$$R{-}Ø\bullet + \bullet Ø{-}R \rightarrow R{-}Ø{-}Ø{-}R \quad (4)$$

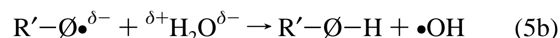
Depending on the dipole orientation of the intermediate species eq 1, reaction with the molecules of the solvation shell (water) may occur via eq 5a and b, where R and R′ are the electron acceptor (e.g., nitro) or electron donor group (e.g., methoxy), respectively. The type of group (R or R′) has an influence on the type of side reaction and on the reorganization of the solvation shell after the electron transfer process. The charge distribution among the phenyl ring changes, and the former positively charged carbon atom (where the diazo group was located) becomes slightly negative. This behavior is expressed by a change in the dipole orientation, as calculated for the transformation of 4-MeBDT to 4-MeB.[8]

A possible side reaction with the solvent (water) for electron acceptor groups (e.g., nitro) is:



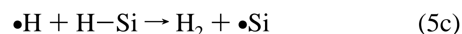
$$R{-}Ø\bullet^{\delta+} + {}^{\delta-}OH_2^{\ \delta+} \rightarrow R{-}Ø{-}OH + \bullet H \quad (5a)$$

A possible side reaction with the solvent (water) for electron donor groups (e.g., methoxy) is:

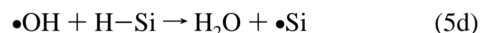


$$R'{-}Ø\bullet^{\delta-} + {}^{\delta+}H_2O^{\delta-} \rightarrow R'{-}Ø{-}H + \bullet OH \quad (5b)$$

H atoms or OH radicals may now capture an H atom from the hydrogenated Si surface, as outlined for the phenyl radical in eq 2, and in turn, a dangling bond is formed (eq 5, parts c and d, respectively).



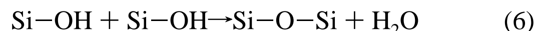
$$\bullet H + H{-}Si \rightarrow H_2 + \bullet Si \quad (5c)$$



$$\bullet OH + H{-}Si \rightarrow H_2O + \bullet Si \quad (5d)$$

This dangling bond is now able to capture additionally a phenyl ring species via eq 3.

However, Si dangling bonds may react with OH radicals and water molecules so that Si−OH is formed. At least, Si−OH bonds may condense to Si−O−Si, as outlined in reaction 6 and, consequently, lead to the formation of SiO_2 surface species.



$$Si{-}OH + Si{-}OH \rightarrow Si{-}O{-}Si + H_2O \quad (6)$$

There is another H atom source: positively charged and solvated protons from the acidic aqueous solution even at a high concentration. These protons can capture an electron and form H atoms near the Si surface (eq 7), which finally react with an unsaturated Si bond, leading to a new reactive Si−H surface site for the grafting process as needed in eq 2.

$$H^+ + e^- \rightarrow \bullet H \quad (7)$$

In the next two subsections, we will discuss the observed results of I_{PL} and U_{PV} with respect to competing side reactions with water molecules.

(b) Grafting of Nitrobenzene in the Presence of Water. The grafting of 4-NB from 4-NBDT shows a reduction of I_{PL} with increasing negative potential and concentration for the grafting of 4-NB from 4-NBDT (Figure 5). Taking into account that a Si−C bond is not a recombination active defect,[4,8] the change in I_{PL} is correlated to other surface species or complexes such as SiO_x. In the case of 4-NB, the reduction of I_{PL} is not only related to the formation of wet SiO_x at the Si surface, which is known to be a poor passivation layer[16] due to the fact that

the amount of SiO_x (Figure 8) is similar at −0.8 and −1.2 V, respectively. Therefore, it is obvious that this behavior is related to another defect formation process, probably the hydrogen evolution, which increases slightly with increasing cathodic potential. It is well-known that H atoms or H_2 molecules diffuse into bulk Si and form etch pits,[26] and hence, recombination active defects are created which reduces I_{PL}.[27] However, the amount of H-diffusion-related defects is in the range of 10^{12} cm^{-2} and, therefore, too small to change the photovoltage (U_{PV}) remarkably (see Figure 3).

It should be noted that I_{PL} of Si surfaces is sensitive to a recombination center concentration on the order of less than 10^{12} cm^{-2} (i.e., less than one-tenth of a percent of Si surface bonds), whereas U_{PV} becomes quite constant when most of the possible 50% of the Si(111) surface bonds (about 3.5×10^{14} cm^{-2}) are grafted. Additionally, the IR ellipsometric sensitivity is in the monolayer regime (depending on the oscillator strength of the respective surface bond), and therefore, changes of a 1/1000 of a monolayer as observed in PL may not be detected by changes in IR ellipsometric data.

(c) Grafting of Methoxybenzene in the Presence of Water. The behavior of U_{PV} and I_{PL} is completely different during grafting of 4-MeB from 4-MeBDT in an aqueous solution (Figures 4 and 6). The less-reduced I_{PL} at −1.2 V with respect to the value at −1 V is obviously related to a decrease in the amount of wet SiO_x surface species (see Figure 9), which are known to be recombination active centers as outlined above. Additionally, a reduction of SiO_x surface species implies a reduced amount of Si−OH surface intermediate species during the grafting process. Si−OH surface bonds induce a negative surface charge, and consequently, the change in band bending of p-Si is less pronounced at a more positive potential (e.g., at −1 V instead of −1.2 V in Figure 4A) as observed from our PV measurements. A similar effect is observed when the concentration of 4-MeBDT is changed from 5 to 1 mmol for the grafting process (Figure 4B).

(d) Thermodynamic Considerations. From recent grafting experiments on *n*-TiO_2 samples, it is known that the redox potential (U_{redox}) of 4-MeBDT/4-MeB (Me*) is about 170 mV cathodic from U_{redox} of the 4-NBDT/4-NB (N*) couple.[28] Hydrogen evolution was observed to be slightly cathodic from the Me* redox system. However, the potential distribution of these redox pairs is quite broad (about 200 mV).[28] Figure 10 shows a sketch of the energetic positions U_{redox} of Me*, N*, and H^+/H in solution with respect to the valence and conduction band (E_V and E_C) of p-Si at different polarization in the dark ((−−) −1 V; (- - -) −1.2 V). The thickness of the arrows denotes the intensity of current density without consideration of any kinetic hindrance. The electron transfer from p-Si to 4-NBDT is thermodynamically favored with respect to the more cathodically shifted H^+/H redox couple, independent of the applied potential. In comparison, the electron transfer to 4-MeBDT competes with the H^+/H redox system, even due to the high concentration of H^+ ions in the acidic solution. The electron transfer to the H^+/H system is preferred at a more cathodic potential of −1.2 V and should, therefore, lead to a higher amount of H atoms on the surface (H^S). These H^S atoms can react with intermediate Si dangling bonds to form Si−H bonds, which are known to be the best species to passivate Si(111) surfaces,[29−31] and hence, the relative reduction of I_{PL} (δI_{PL}) is less pronounced, as observed by our PL measurements (Figure 6A). The formation of H^S atoms has an influence on the competing reaction, especially during grafting of 4-MeB from 4-MeBDT, which has a U_{redox} closer to the H^+/H system

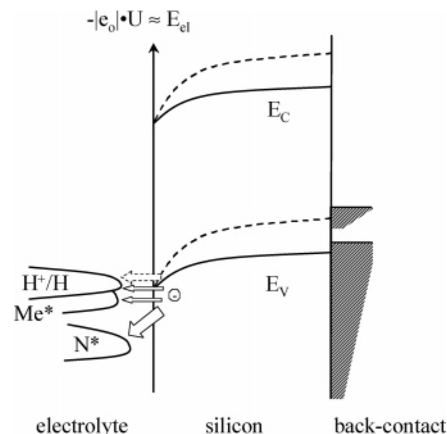


Figure 10. Schematic sketch of the energetic positions U_{redox} of (Me*) 4-MeBDT/4-MeB, (N*) 4-NBDT/4-NB, and H^+/H_2 in solution with respect to the valence and conduction band (E_V and E_C) of p-Si at different polarization in the dark ((−−) −1 V; (- - -) −1.2 V).

with respect to the N* couple. Thus, the amount of direct attacks of Si dangling bonds by oxygen-containing species (H_2O, OH radical) is reduced during the grafting of 4-MeB. This behavior is reflected by a strongly reduced amount of SiO_x surface species (Figure 8A) and a slightly higher amount of Si−H surface bonds (Figure 8B) at −1.2 V in comparison to −1 V for the grafting of 4-MeB.

However, no strong influence on the amount of SiO_x or 4-NB surface species was observed for grafting of 4-NB from 4-NBDT (Figure 8A and B).

Conclusions

We have shown that the basic chemical reaction at the Si surface which leads to the grafting of phenyl monolayers does not influence the surface recombination velocity. Nonradiative defects are mainly formed at the Si surface by side reactions with the solvent (water) during the electrochemical grafting of organic monolayers. The influence of side reactions can be reduced by the appropriate choice of the grafting condition: moderate concentration and moderate or strong cathodic potential should be used (depending on the redox potential). Additionally, our results show that the grafting of diazonium compounds is a complex radical reaction where the solvent (here water) plays an important role for the electronic and chemical passivation of the Si/organic layer interface. The radicals possibly react with water molecules. However, radicals of NB and MeB have different charges close to the radical position. As a result, H or OH radicals are received as products from different reactions with the solvent (eq 5a and b). These radicals are able to react with Si surfaces. In the case of NB, a H atom reacts, which can be exchanged by an organic molecule. In the case of MeB, an OH radical reacts with the Si surface. This is not a reversible reaction, and the rate of this undesirable reaction decreases with increasing cathodic potential. The formation of oxides can be suppressed in the presence of electrochemically induced surface H atoms.

However, other types of side reactions, e.g., reaction of radicals with ions from supporting electrolyte (SO_4^{2-}) or Si dangling bonds with an excited intermediate state of an uncharged diazonium compound (N_2−Ø−R), which may lead to the formation of Si−N bonds, should be investigated.

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References and Notes

(1) Strother, T.; Hamers, R. J.; Smith, L. M. *Nucl. Acids. Res.* **2000**, *28*, 3535.

(2) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; Leeuw, D. M. d. *Nature* **1999**, *401*, 685.

(3) Cohen, R.; Ashkenasy, G.; Shanzer, A.; Cahen, D. Semiconductor Electrodes Photoelectrochemistry. In *Grafting Molecular Properties onto Semiconductor Surfaces*; Wiley-VCH: Weinheim, 2002; Vol. 6, Chapter 2.3.

(4) Hartig, P.; Rappich, J.; Dittrich, T. *Appl. Phys. Lett.* **2002**, *80*, 67.

(5) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir−Blodgett to Self-Assembly*; Academic Press: San Diego, CA, 1991; Chapter 3.

(6) Wagner, P.; Nock, S.; Spudich, J. A.; Volkmuth, W. D.; Chu, S.; Cicero, R. L.; Wade, C. P.; Linford, M. R.; Chidsey, C. E. D. *J. Struct. Biol.* **1997**, *119*, 189.

(7) Wayner, D. D. M.; Wolkow, R. A. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 23.

(8) Hartig, P.; Dittrich, T.; Rappich, J. *J. Electroanal. Chem.* **2002**, *524−525*, 120.

(9) Warntjes, M.; Vieillard, C.; Ozanam, F.; Chazalviel, J. N. *J. Electrochem. Soc.* **1995**, *142*, 4138.

(10) Villeneuve, C. H.; Pinson, J.; Ozanam, F.; Chazalviel, J. N.; Allongue, P. *Mater. Res. Soc. Symp. Proc.* **1997**, *451*, 185.

(11) Fidélis, A.; Ozanam, F.; Chazalviel, J.-N. *Surf. Sci.* **2000**, *444*, L7.

(12) Hurley, P. T.; Ribbe, A. E.; Buriak, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 11334.

(13) Rappich, J.; Hartig, P.; Nickel, N. H.; Sieber, I.; Schulze, S.; Dittrich, T. *Microelectron. Eng.* **2005**, *80*, 62.

(14) Kronik, L.; Shapira, Y. *Surf. Sci. Rep.* **1999**, *37*, 1.

(15) Timoshenko, V. Y.; Petrenko, A. B.; Stolyarov, M. N.; Dittrich, T.; Fuessel, W.; Rappich, J. *J. Appl. Phys.* **1999**, *85*, 4171.

(16) Dittrich, T.; Burke, T.; Koch, F.; Rappich, J. *J. Appl. Phys.* **2001**, *89*, 4636.

(17) Hinrichs, K.; Gensch, M.; Röseler, A.; Esser, N. *J. Phys.: Condens. Matter* **2004**, *16*, 4335.

(18) Angermann, H.; Henrion, W.; Rebien, M.; Zettler, J.-T.; Röseler, A. *Surf. Sci.* **1997**, *388*, 15.

(19) Higashi, G. S.; Becker, R. S.; Chabal, Y. J.; Becker, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1656.

(20) Röseler, A. *Thin Solid Films* **1993**, *234*, 307.

(21) Gensch, M.; Hinrichs, K.; Röseler, A.; Korte, E. H.; Schade, U. *Anal. Bioanal. Chem.* **2003**, *376*, 626.

(22) Balfour, W. J. *Spectrochim. Acta, Part A* **1983**, *39*, 795.

(23) Plumb, R. C.; Hornig, D. F. *J. Chem. Phys.* **1955**, *23*, 947.

(24) Yota, J.; Burrows, V. A. *J. Appl. Phys.* **1991**, *69*, 7369.

(25) Gensch, M.; Roodenko, K.; Hinrichs, K.; Hunger, R.; Güell, A. G.; Merson, A.; Schade, U.; Shapira, Y.; Dittrich, Th.; Rappich, J.; Esser, N. *J. Vac. Sci. Technol., B* **2005**, *23*, 1838.

(26) Mierry, P. d.; Etcheberry, A.; Rizk, R.; Etchegoin, P.; Aucouturier, M. *J. Electrochem. Soc.* **1994**, *141*, 1539.

(27) Rappich, J.; Dittrich, T.; Timoshenko, Y.; Beckers, I.; Fuhs, W. *Mater. Res. Soc. Symp. Proc.* **1997**, *452*, 797.

(28) Merson, A.; Dittrich, T.; Zidon, Y.; Rappich, J.; Shapira, Y. *Appl. Phys. Lett.* **2004**, *85*, 1075.

(29) Yablonovich, E.; Allara, D. L.; Chang, C. C.; Gmitter, T.; Bright, T. B. *Phys. Rev. Lett.* **1986**, *57*, 249.

(30) Rauscher, S.; Dittrich, T.; Aggour, M.; Rappich, J.; Flietner, H.; Lewerenz, H. J. *Appl. Phys. Lett.* **1995**, *66*, 3018.

(31) Angermann, H.; Kliefoth, K.; Flietner, H. *Appl. Surf. Sci.* **1996**, *104−105*, 107.