Effects of Organic Monolayer Formation on Electrochemiluminescence Behavior of Porous Silicon

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The effects of various organic monolayers on the surface of porous silicon on the electrochemiluminescence (ECL, also referred to as electroluminescence in the literature) characteristics were investigated. Surfaces were terminated with alkyne, alkene, and alkyl functionalities through cathodic electrografting (CEG), Lewis acid-mediated hydrosilylation (LA), and anodic electrografting (AEG), respectively. ECL was induced through the known formic acid/sodium formate electron injection system. Alkyl-terminated surfaces produced through AEG yielded the brightest emission of any of the functionalized surfaces although ECL emission was about half as intense as that from the underivatized Si−H-terminated surface. The lifetime, however, was extended by a factor of 2, and these surfaces demonstrate an unprecedented recharging phenomenon. When ECL ceases, a brief 10 s application of a cathodic bias restores most of the ECL emission intensity. This process can be cycled about 10 times, and results in a substantially greater light output than that from any of the surfaces examined here, including the Si−H-terminated surface. Dodecenyl-terminated surfaces, produced through Lewis acid-mediated hydrosilylation of 1-dodecyne, show the greatest lifetimes, an order of magnitude longer than that of an Si−H-terminated surface, but their emission intensity is unfortunately very low. The induction times for light emission to occur decreased for all the functionalized surfaces, as compared to the native Si−H surface. Explanations for the effects of organic monolayer formation on ECL observed here are described.

Introduction

Since the discovery of photoluminescent light emission (PL) from porous silicon by Canham in 1990,[1] there have been intense research efforts worldwide to prolong and stabilize the LED characteristics of this material.[2] After the subsequent publication of electrochemiluminescence (ECL) of porous silicon in 1991,[3] its many potential applications and uses for silicon-based optoelectronics elicited enormous excitement, but 10 years later, no commercial applications utilizing the light-emitting properties exist. ECL of porous silicon, more so than PL, has been fraught with seemingly insurmountable problems, such as low quantum efficiencies (<1%) and short lifetimes. As a result, the number of porous silicon papers addressing photoluminescence in the recent literature is about 3-fold higher than the number of ECL-based papers. Stable ECL in porous silicon is a very elusive goal, but the attainment of such would be of immense interest since external photoexcitation is not required, as in the case of photoluminescence.

Early work investigating the ECL of porous silicon involved hole injection into the valence band of the material through the decomposition of $Na_2S_2O_8$ in an H_2SO_4 electrolyte, with application of a negative bias to the porous silicon.[4−6] Recombination of the hole and an electron (from the negative applied potential) in a nanocrystallite embedded in the porous silicon matrix results, in a small fraction of the time, in the production of a photon of visible light, leading to the observed ECL. Efficiencies of up to 0.1% have been observed under low cathodic bias conditions (a few volts).[4] Under anodic conditions, however, the emission intensity is 10 times greater, but irreversible oxidation results in a rate of emission decrease ~3 orders of magnitude faster due to formation of a thick oxide layer that effectively shuts down the reaction. The actual mechanistic details are still the source of substantial debate.

More recently, Sailor and co-workers have investigated anodic visible light emission using the decomposition of formic acid as an electron source;[7] application of a positive bias to the porous silicon results in ECL due to recombination of the electrons and holes in the valence band of nanocrystallites within the porous silicon skeleton. This approach has led to a remarkably longer ECL lifetime, as compared to those of other

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(1) Canham, L. T. *Appl. Phys. Lett.* **1990**, *57*, 1046.

(2) Hirschman, K. D.; Tsybeskov, L.; Duttagupta, S. P.; Fauchet, P. M. *Nature* **1996**, *384*, 338.

(3) Halimaoui, A.; Oules, C.; Bomchil, G.; Bsiesy, A.; Gaspard, F.; Herino, R.; Ligeon, M.; Muller, F. *Appl. Phys. Lett.* **1991**, *59*, 304. We prefer the term "electrochemiluminescence" to "electroluminescence" since a chemical reaction must occur to induce light emission, in tandem with the applied potential.

(4) Canham, L. T.; Leong, W. Y.; Beale, M. I. J.; Cox, T. I.; Taylor, L. *Appl. Phys. Lett.* **1992**, *61*, 2563.

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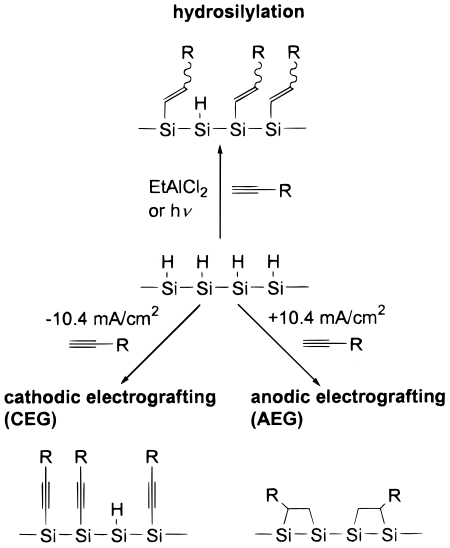

Figure 1. Schematic of the surface chemistry approaches utilized in this paper. Hydrosilylation of alkynes results in an alkenyl-terminated surface. Cathodic electrografting (CEG) takes place upon application of a negative bias to the porous silicon, and produces an alkyne-based monolayer. Anodic electrografting (AEG) results in an alkyl-terminated surface which may contain bis-silylated derivatives, and saturated oligomeric fragments.

anodically biased systems, but burn-out of the porous silicon occurs within approximately 30 min, and there is a substantial delay (induction period) before light emission occurs. The cause for termination of light emission is not yet clear, but is most likely due to oxidation of the surface, as occurs with photoluminescence and hole injection-based ECL.

Since oxidation of the porous silicon appears to be involved in cessation of the light-emitting characteristics of porous silicon, we decided to investigate the effects of surface functionalization on the lifetime and induction time of ECL. Previously, our group had demonstrated that hydrosilylation of alkynes and alkenes on a silicon hydride-terminated surface leads to dramatically stabilized surfaces, due to formation of a protective organic monolayer.[8−10] Several of these derivatized surfaces are chemically robust, and are capable of withstanding extended caustic alkali treatment (pH 12, 30 min), with no apparent oxidation. Hydrosilylation is mediated by the Lewis acid $EtAlCl_2$[8] (referred to as LA) or, for photoluminescent samples, is promoted with simple illumination of white light of moderate intensity.[9] More recently we found that cathodic or anodic electrografting of alkynes also results in formation of stable organic monolayers on the porous silicon surface.[10] This collection of functionalization methodologies, outlined in Figure 1, permits termination with unconjugated (i.e., alkyl) and conjugated (i.e., styrenyl) moieties, hydrophilic and hydrophobic ω-groups (i.e., hydroxy and aliphatic, respectively), perfluorinated alkyls, and a host of other possibilities. The surface characteristics can be modulated and tailored upon demand.

In this paper, we investigate the effects of surface derivatization on electron injection-based ECL. Because solution-deposited films of calixarenes on porous silicon surfaces have been shown to increase the lifetime of ECL from porous silicon, it is possible that nanometer-thick, packed hydrophobic monolayers might also modulate light emission.[11] Indeed, varying the surface characteristics has enormous effects on the observed light emission characteristics of the material, including influences on lifetime, induction time, and intensity, all of which are described here. To the best of our knowledge, this represents the first time the effect of organic monolayers on ECL has been investigated.

Experimental Section

The porous silicon (PS) samples used in all experiments were prepared from polished crystalline silicon wafers (highly Sb doped n-type, 0.008−0.020 Ω·cm). The etching was carried out in an ethanoic HF solution (1:1 48% aqueous HF/EtOH) with a 1.15 cm^2 area exposed for 3 min at 74 mA/cm^2 current density and with white light illumination of ∼25 mW/cm^2 from an ELH W bulb (300 W, General Electric).[12] The etched silicon, still in the etching cell, was fully washed with EtOH and pentane and then dried under N_2 flow. The final check for the successful preparation of PS was done by illumination with a hand UV lamp to show the characteristic orange color of photoluminescence.

Lewis Acid-Mediated Reaction. Functionalization of the PS was performed by addition of 50 μL of a commercial 1.0 M hexane solution of $EtAlCl_2$ to a 1.15 cm^2 area of porous silicon followed by 150 μL of substrates (1-dodecyne, 1-pentyne, phenylacetylene) in a nitrogen-filled glovebox.[8] The substrates were allowed to react for 1 h for alkynes and 12 h for alkenes. The functionalized PS samples were taken out of the box, washed with excess DCM (dichloromethane), THF (tetrahydrofuran), water, EtOH, and pentane, and then dried under a nitrogen stream.

White Light Chemistry. The neat substrate (150 μL) was added directly to the PS surface in a nitrogen-filled glovebox. A ChemGlass window (borosilicate) was sealed with a Viton O-ring over the etching cell reservoir and clamped to maintain the nitrogen atmosphere over the surface. The setup was removed from the box, and then irradiated with the W source through the window for 1 h.[9]

Cathodic and Anodic Electrografting. Electrografting on the PS was carried out using the same electrochemical setup as for the etching samples.[10] This reaction is performed under a nitrogen environment. The electrolyte solution (1.5 mL, 1.0 M $n\mathrm{Bu_4NPF_6}$ in DCM) was added to the sample still in the etching cell, followed by 100 μL of 1-dodecyne. CEG was performed under −10.4 mA/cm^2 current flow for 120 s (the PS electrode was negatively charged and the counter electrode (Pt) positively charged). AEG was performed in an identical manner except the polarization of the electrodes was reversed (+10.4 mA/cm^2 for 120 s; the PS electrode was positively charged and the counter electrode negatively charged). Following completion of the reaction, the samples were washed with fluent DCM, THF, EtOH, and pentane, and dried under nitrogen. The samples prepared by all of the methods were kept in the glovebox before use to protect them from contact with the atmosphere.

Electrochemiluminescence. A 1.0 M NaCOOH electrolyte solution in HCOOH was used as an electron injection source in the etching cell containing the functionalized PS sample.[7] An anodic bias was placed on the silicon electrode (+3.00 V, self-referenced). Emitted light was captured through

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(8) (a) Buriak, J. M.; Allen, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 1339. (b) Buriak, J. M.; Stewart, M. P.; Geders, T. W.; Allen, M. J.; Choi, H. C.; Smith, J.; Raftery, D.; Canham, L. T. *J. Am. Chem. Soc.* **1999**, *121*, 11491.

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(12) Lee, E. J.; Bitner, T. W.; Ha, J. S.; Shane, M. J.; Sailor, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 5375.

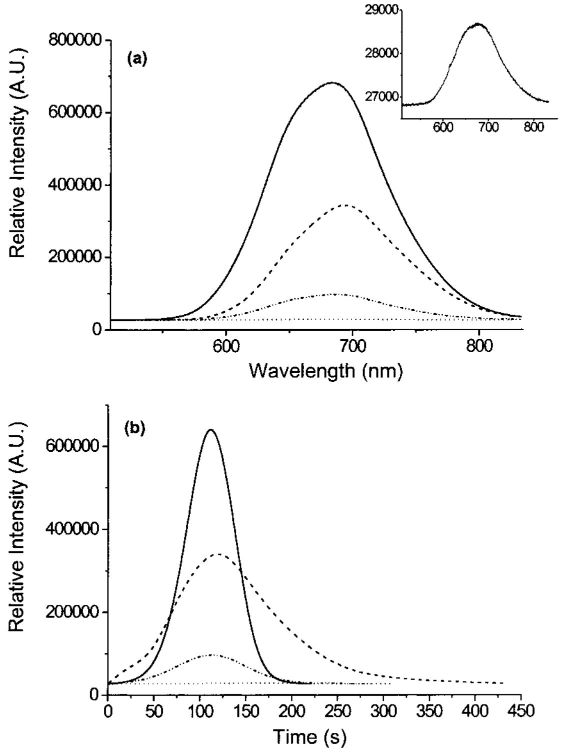

Figure 2. ECL profiles of Si−H and covalently functionalized surfaces with respect to (a) wavelength (nm) and (b) time (s). The solid line represents the normal Si−H surface, the long-dashed line the AEG 1-dodecyne-functionalized surface, the short-dashed line the CEG 1-dodecyne-functionalized surface, and the dotted line the Lewis acid-mediated 1-pentyne-functionalized surface. The inset of (a) is the magnified ECL emission profile of the Lewis acid-mediated 1-pentyne-functionalized surface.

the a 490 nm LWP filter (CVI LO490) into an Acton Research Spectra Pro 275 monochromator (0.275 m) and a Princeton Instruments CCD detector (LN/CCD-1024-E/1) cooled with liquid nitrogen.

Results

Conditions similar to those described by Sailor and co-workers for electron injection-based ECL using a sodium formate/formic acid system were utilized on porous silicon produced from n$^+$-type single-crystal silicon.[7] Aqueous KCl and HCl (1.0 M) electrolytes also show ECL light emission, presumably due to ionization and oxidation of surface silicon atoms to silicon dioxide,[13] but the intensity is substantially lower and rather heterogeneous and patchy across the face of the porous silicon wafer. The formic acid system, however, produces a very consistent bright orange emission across the surface of the porous silicon sample and was utilized throughout this study. Thus, anodic ECL may arise from injection of electrons into the conduction band of silicon nanocrystallites generated not only by formic acid dissociation, but also through surface oxidation. To investigate the influence of both the nature of the organic termination and the functionalization approach on ECL efficiency as compared to that of the unfunctionalized Si−H-terminated surface, a number of surfaces with different covalently bound moieties were studied at a constant potential of +3.00 V using the sodium formate/formic acid electrolyte. This potential was chosen since voltage/light emission curves indicate that ECL occurs only at a minimum voltage of +2.75 V with this electrolyte combination in our system. In the absence of a sodium salt, voltages exceeding +10 V are required for light emission. Changes in current density

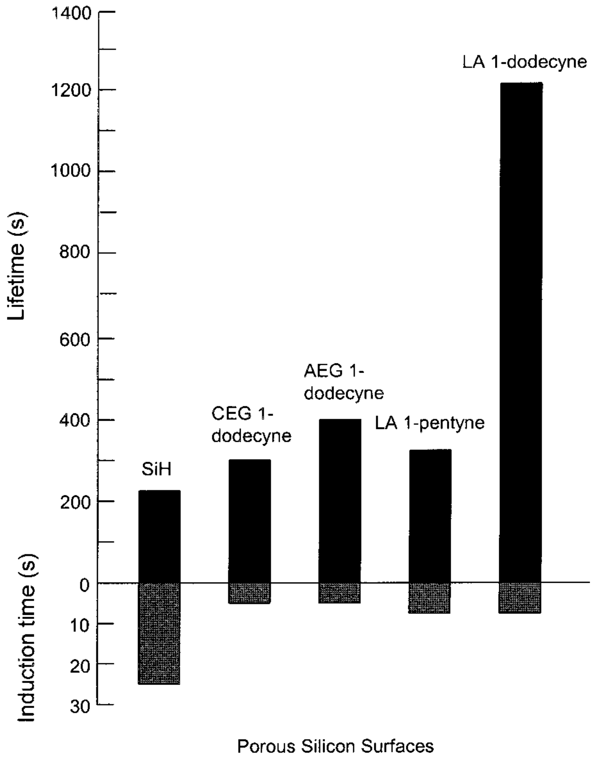

Figure 3. Comparison of overall lifetimes and induction times of various surfaces.

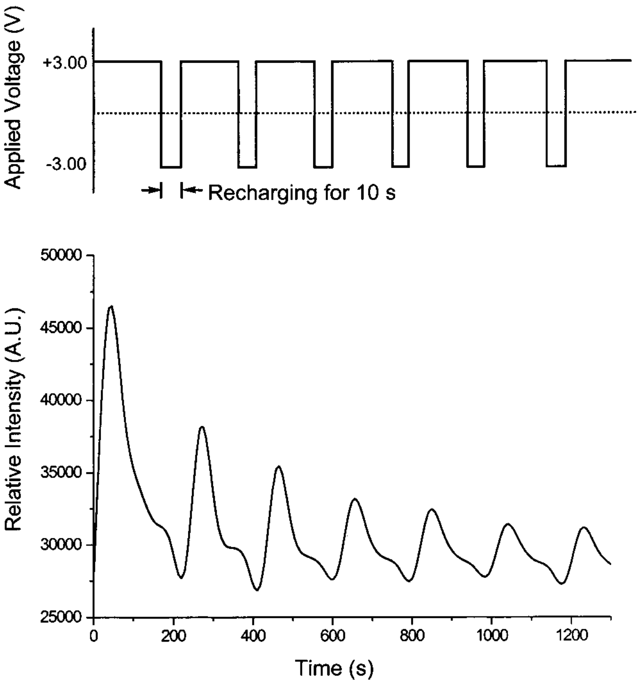

Figure 4. Recharging phenomena observed when the AEG 1-dodecyne-functionalized surface is submitted to ECL conditions. The small shoulder at the end of each cycle corresponds to the point where the polarity is switched back to the negative bias.

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(13) Goryachev, D. N.; Belyakov, L. V.; Sreseli, O. M.; Polisskii, G. *Semiconductors* **1998**, *32*, 529.

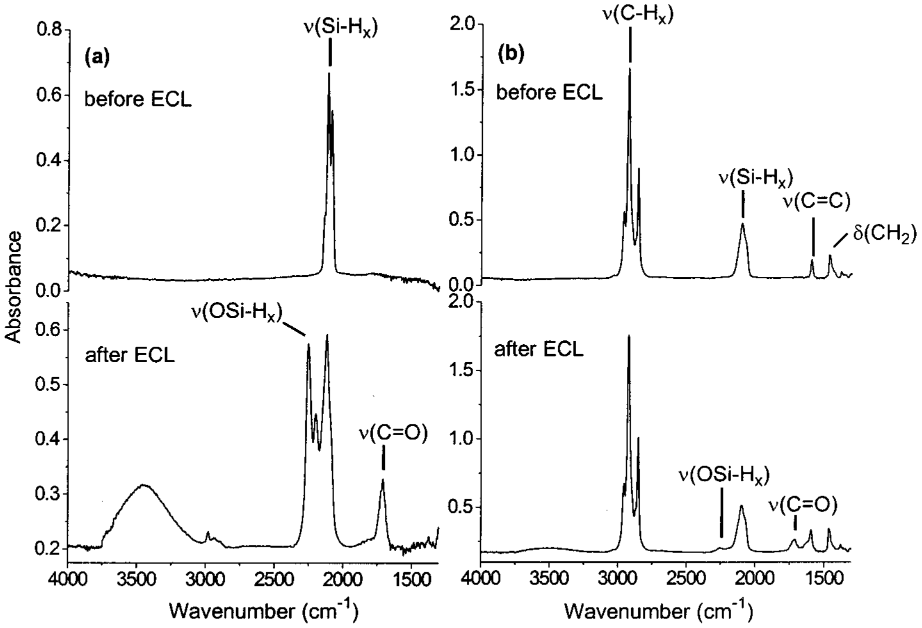

Figure 5. Comparison of transmission FTIR spectra before and after ECL: (a) normal Si−H-terminated surface and (b) Lewis acid-mediated 1-dodecyne-functionalized surface.

during these potentiostatic experiments were monitored and were similar to those observed by Sailor and co-workers:[7] a small increase is observed after commencement of ECL, followed by a constant decay. As shown in Figure 2, different functionalization methodologies lead to dramatically different ECL characteristics.

Electrografting Approaches. The cathodic and anodic electrografting methodologies result in retention of a substantial fraction of ECL emission intensities, with the anodic electrografting of 1-dodecyne showing greater than 50% the brightness of an Si−H-terminated surface. Interestingly, although some quenching was observed, the lifetime of light emission was increased by approximately a factor of 2, as can be seen in Figures 2b and 3. The wavelength maximum of emission (690 nm) is unaffected by functionalization; no major shifts are observed. All the derivatizations resulted in a substantial lowering of the induction time. Under our conditions, light emission of an Si−H-terminated surface does not commence for 12−20 s after application of the bias to the surface (Figure 3). In all cases, with the functionalized surfaces, however, ECL begins in 2−6 s, regardless of the surface chemical approach taken.

In the case of AEG, a remarkable recharging phenomenon was observed. In all previously studied cases both in our laboratory and in the literature,[4−7] after termination of ECL from a porous silicon sample, no further light emission was possible, probably due to oxidation and destruction of the active nanocrystallites in the porous silicon skeleton. When 1-dodecyne is electrografted to the porous silicon surface through AEG, however, the sample may be recharged to emit light multiple times (Figure 4). During ECL, the light intensity drops to almost zero; at this point, a 10 s application of 3.00 V of the opposite potential (cathodic bias), followed by return to an anodic potential of 3.00 V, results in instantaneous resumption of light emission. As demonstrated in Figure 4, this recharging can be recycled up to 10 times, with a slightly decreasing maximum intensity each time. The total lifetime for the recharged porous silicon sample, about 30 min, is increased by a factor of approximately 7 over that for an unfunctionalized (Si−H) porous silicon sample.

Hydrosilylation Approaches. When an aliphatic alkyne, either 1-dodecyne or 1-pentyne, is hydrosilylated through the Lewis acid-mediated reaction, yielding dodecenyl or pentenyl-terminated surfaces, respectively, the emission intensity is almost unobservable with our CCD setup as compared to that from the Si−H control. These samples exhibited the lowest brightness of this study, although the red color of ECL can be clearly observed by the naked eye in a darkened room. The inset in Figure 2 portrays the low intensity of ECL for a 1-pentyne-functionalized surface. A styrenyl-terminated surface, produced through hydrosilylation of phenylacetylene, however, shows absolutely no light emission whatsoever. Photoluminescence is also known to be quantitatively quenched by this conjugated termination and other closely related conjugated aryls, suggesting that this class of organic fragments act as sites of nonradiative recombination in both ECL and PL manifolds.[14] Lewis acid-mediated hydrosilylation of alkenes was also examined as it produces an alkyl-terminated surface as opposed to an alkenyl-terminated surface. A dodecyl-derivatized surface, formed through this route, similarly results in ECL of low intensity. While the ECL emission intensity of the dodecenyl- and dodecyl-terminated surfaces was very low, the lifetimes were extended by an order of magnitude (Figure 3). Lowered induction times were also observed, as is the case with the electrografting approaches. The white-light-promoted hydrosilylation of alkynes on porous silicon resulted in patchy and inhomogeneous ECL and was not studied further.

Discussion

The effects on ECL could be due to a number of different factors, including steric inaccessibility of the

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electrolyte to the porous silicon nanocrystallites, reduced wetting of the surface due to incorporation of hydrophobic groups, and changes in the electronic nature of the nanocrystallites, for instance. Because of the increased chemical stability of the hydrophobic surfaces terminated with long alkyl chains, the increased lifetime may be due to decreased surface oxidation of the nanocrystallites. FTIR studies indicate that the extent of oxidation of the functionalized surfaces is lessened as compared to that of an Si—H-terminated sample. As clearly demonstrated by Sailor and co-workers, the appearance of oxygen-back-bonded Si—H groups at 2260 $\mathrm{cm^{-1}}$ and silyl ester moieties [ν(C═O) at 1717 $\mathrm{cm^{-1}}$] following ECL is the result of important changes in the surface characteristics of the material.[7,12] In a porous silicon sample terminated with dodecenyl groups through Lewis acid-mediated hydrosilylation, however, the oxygen-back-bonded Si—H and ν(C═O) vibrations due to surface oxidation and silyl formyl esters are minor, as shown in Figure 5. These results suggest that the dodecenyl-terminated surface has both a longer lifetime and a diminished intensity due to inaccessibility of the corroding electrolyte under these conditions.

If inaccessibility of the sodium formate electrolyte and its inability to pass through the hydrophobic monolayer on the nanocrystallite surfaces are the cause of the diminished ECL intensity, then a more hydrophobic salt could perhaps aid in charge transfer. Halimaoui has shown that wettability has very strong effects on ECL and the chemical etch rate of porous silicon structures. Because the long alkyl chain monolayers are highly hydrophobic, it may be that the electrolyte has difficulty penetrating the pores.[15] 15-Crown-5, a crown ether with high propensity to bind to sodium cations, was added with the hopes that rendering the cation more hydrophobic would improve the ECL. Surprisingly, for both functionalized and Si—H-terminated samples, all light emission was shut down upon the addition of 1 or more equiv of 15-crown-5. If ECL was commenced and then 2 equiv of 15-crown-5 added per sodium cation, all light emission ceased; addition of excess sodium formate/formic acid electrolyte brought about a return of ECL, which could in turn be shut down again by addition of 1 equiv of 15-crown-5. These results suggest that direct binding of the cation to the formate anion through a Na—O bond is crucial for its decomposition. If the organic cation tetramethylammonium ($\mathrm{NMe_4^+}$) is used, ECL does not take place, which substantiates the assumption that strong binding between the cation and formate is essential to assist in $^{\bullet}\mathrm{CO_2^-}$ formation and subsequent electron injection. With this large organic cation, only ion pair formation can occur as opposed to a direct bond with the formate anion. Ammonium ($\mathrm{NH_4^+}$), on the other hand, does permit ECL, presumably due to its ability to bind to formate through a hydrogen bond of the form N—H—O.

A tris(ethylene)glycol-terminated surface was prepared through Lewis acid-mediated hydrosilylation of tris(ethylene)glycol vinyl ether since this surface would permit facile penetration and binding of the sodium cations. Unfortunately, due to the low stability of these surfaces to water and chemical attack, the ECL did not improve. These surfaces are clearly very hydrophilic as they are wetted easily by water, which renders them more sensitive, as opposed to the hydrophobic monolayer-coated samples.

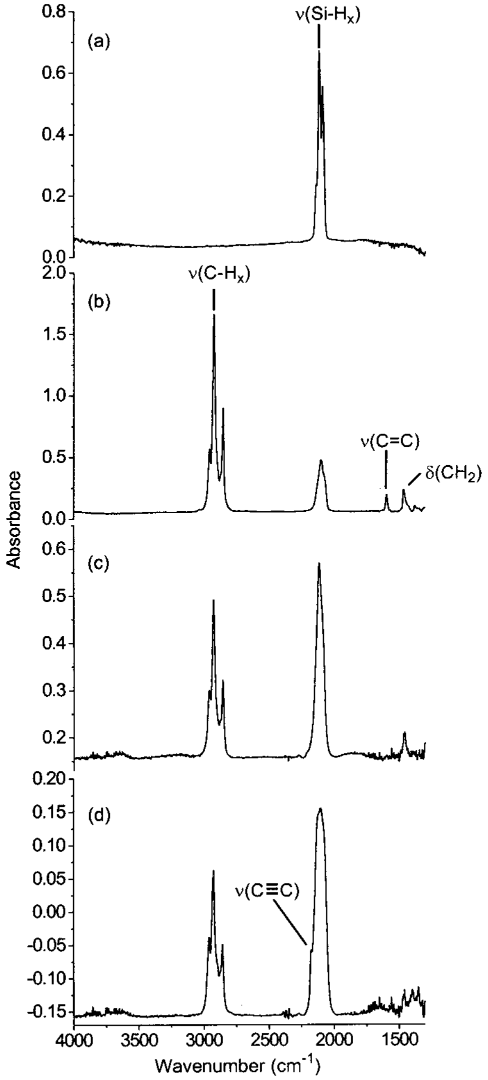

Figure 6. Transmission FTIR spectra of porous silicon after functionalization through various methods: (a) Si—H-terminated surface, (b) Lewis acid-mediated 1-dodecyne-functionalized surface, (c) AEG 1-dodecyne-functionalized surface, and (d) CEG 1-pentyne-functionalized surface.

FTIR studies show that those surfaces with a lower concentration of organic groups have shorter lifetimes. By comparing the ratio of ν(C—H) at ~2800—3000 $\mathrm{cm^{-1}}$ and residual ν(Si—H) centered around ~2100 $\mathrm{cm^{-1}}$, relative coverages can be inferred. The dodecenyl surface, produced through Lewis acid-mediated hydrosilylation (Figure 6b), has the highest ratio, indicating the most complete coverage as compared to that of the other preparation methods. Because it shows the lowest emission intensity and longest lifetime, it indicates that coating the porous silicon surface with a hydrophobic layer protects the surface but reduces the electrical contact necessary for bright ECL. The 1-dodecyne-functionalized AEG surface (Figure 6c) has a substantially lower ν(C—H)/ν(Si—H) ratio, which results in a shorter lifetime due to chemical decomposition of the surface as compared to that of the dodecenyl-terminated

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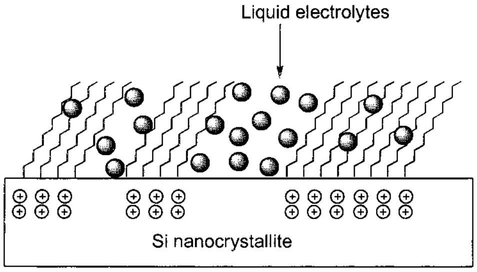

Figure 7. Proposed rearrangement of h^{+}'s within a silicon nanocrystallite due to the inductive effect of the surface Si−C bonds.

surface produced through the Lewis acid chemistry, but brighter ECL due to better electrolyte contact.

In all cases, a reduced induction time was observed when the porous silicon surface was functionalized with organic moieties. One possible explanation is the inductive effect of the alkyl, alkenyl, or alkynyl groups on the silicon nanocrystallite surface. Figure 7 shows a schematic of this proposed effect and indicates how it might result in localization of holes (h^{+}'s) on the silicon surface. Increased electron density on the surface of the nanocrystallites influences their band gap energy, causing localization of the holes which were previously more evenly dispersed on the unfunctionalized Si−H-terminated silicon surface. Therefore, recombination of holes (in the valence band) and electrons (injected into the conduction band through formate decomposition) occurs more rapidly. In the case of Si−H-terminated porous silicon, some surface oxidation must occur before ECL gets underway; oxidation produces Si−O bonds on the surface which may assist in localizing holes on the surface in a similar manner. The time taken to produce sufficient numbers of Si−O bonds on the surface to induce hole localization may constitute some or all of the observed induction time. The mechanism for the recharging effect observed from the surface prepared by AEG with 1-dodecyne is still under investigation. The decrease of the degradation of ECL may be due to liberation of hydrogen during cathodization and hydrogen adsorption on nanocrystallite surfaces, as suggested by Goryachev and co-workers.[13] Another possible explanation to be considered is an overshoot phenomenon which acts as a charge storage process during application of the negative bias.[16]

Conclusions

These studies indicate that functionalization of the surface of porous silicon with organic monolayers can have important effects on the ECL characteristics. Anodically electrografted surfaces coated with alkyl subsituents show the brightest ECL of the modified surface, and a lifetime twice that of a Si−H-terminated surface. The organic monolayers appear to have both steric and electronic effects on ECL: the densest monolayers prevent good electrical contact between the electrolyte and the nanocrystallites, but protect the surface from degradation, leading to an extended lifetime but low light emission. The organic moieties covalently bonded to the surface affect the electronics by assisting hole localization at the surface, which reduces the induction or waiting time normally seen in porous silicon ECL. The fascinating phenomenon of recharging through application of a cathodic potential may open new windows for both optoelectronics and fundamental studies into the nature and mechanism of ECL.

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