Anodic and cathodic electrografting of alkynes on porous silicon†

Edward G. Robins, Michael P. Stewart and Jillian M. Buriak*

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393 USA. E-mail: buriak@purdue.edu

A versatile electrochemical grafting reaction connects conjugated molecules to porous silicon surfaces with either a positive or negative bias.

Porous silicon, an interconnected network of silicon nanowires and nanocrystallites,[1] is terminated by metastable silicon–hydride groups ($Si-H_x$) and Si–Si bonds. There are now a number of techniques utilized for chemical modification of these species on the surface of porous silicon.[2–6] Using the Si surface as a semiconducting electrode, several workers have reported electrochemical Si–C bond formation by direct grafting, an approach with few parallels to soluble, molecular silane chemistry.[7–9] Herein we report a system for electrochemically grafting terminal alkynes to porous silicon which gives two distinct surface derivatizations, depending on the polarity of the surface bias. *Cathodic* electrografting (CEG) directly attaches alkynes to the surface, whereas *anodic* electrografting (AEG) yields an alkyl surface.
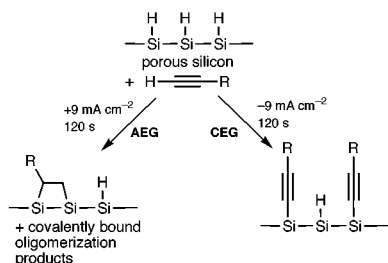
FTIR analysis of phenylacetylene CEG (surface **1**, Fig. SM3†) reveals $Si-H_x$ stretches which are broadened and decreased in integrated intensity compared to unmodified porous silicon. The absence of a $\nu(\equiv CH)$ mode around 3300 cm^{-1} and an observed sharp silylated alkyne $\nu(C\equiv C)$ at 2159 cm^{-1} is consistent with a Si–alkynyl surface and not simple physisorption. For instance, the $\nu(C\equiv C)$ of 1-phenyl-2-(trimethylsilyl)acetylene appears at 2160 cm^{-1} while that of phenylacetylene is observed at 2110 cm^{-1}. Similarly, CEG of dodec-1-yne (surface **2**, Fig. SM1†) shows a $\nu(C\equiv C)$ at 2176 cm^{-1}, which is identical to the silylated molecular analogue 1-trimethylsilyldodec-1-yne at 2176 cm^{-1}; underivitized dodec-1-yne appears at 2120 cm^{-1}. Fig. 1(*a*) shows the pentynyl terminated surface (surface **3**) with the $\nu(C\equiv C)$ at 2179 cm^{-1}. This surface was hydroborated with a 0.5 M THF solution of disiamylborane[10] to verify the presence of the silylated triple bond. The appearance of a broad band at 1580 cm^{-1} and the concomitant consumption of the $\nu(C\equiv C)$ is indicative of a silylated, borylated double bond, which was verified by hydroboration of 1-trimethylsilyldodec-1-yne and subsequent FTIR analysis [$\nu(C=C)$ at 1584 cm^{-1}].

Covalent electrografting of alkynes also appears to occur when an anodic potential is applied, although AEG surfaces show complete reduction of all unsaturated bonds. The C≡C
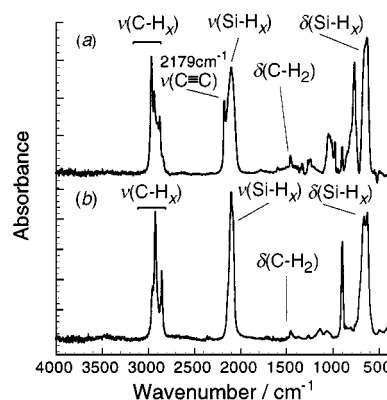
Fig. 1 Transmission FTIR of derivatized porous silicon: (*a*) CEG of pent-1-yne (surface **3**). (*b*) AEG of dodec-1-yne (surface **8**).

triple bond is not observed, with only a weak vibration corresponding to a hydrosilylated double bond mode (1600 cm^{-1}) in the FTIR spectra. In contrast to CEG, AEG of dodec-1-yne [surface **8**, Fig. 1(*b*)] has features relating only to aliphatic C–H bonds. In the spectrum of phenylacetylene AEG (surface **9**, Fig. SM8†), ring breathing modes at 1599, 1493 and 1446 cm^{-1} compare closely with polystyrene films and differ from those observed for the conjugated CEG surface **1** at 1596, 1489 and 1443 cm^{-1}. Boiling of the surfaces functionalized through AEG for 30 min in $CHCl_3$ results in no change in the FTIR spectrum, suggesting covalent bonding as opposed to physisorption. Based on the coincidence of the ring modes and the saturation of the C≡C bonds, we conclude that doubly hydrosilylated (bis-silylation) or possibly oligomeric material decorates the porous silicon surface (*vide infra*).

Photoluminescence (PL) spectra of CEG samples show varying intensities depending on the surface type (Fig. 2). Surfaces **2**–**4** (alkynyl groups) retain between *ca.* 5–15% of the light emission, with a small red shift of *ca.* 10 nm relative to freshly prepared porous silicon ($\lambda_{max} = 663$ nm). The phenethynyl surface **1** and other arynyl terminated surfaces (surfaces **5** and **6**) show no light emission whatsoever, as has been observed by Song and Sailor previously.[5a] Similarly, diphenylphosphinoethynyl surface **7** exhibits complete PL quenching as well. AEG samples have more intense PL, with *ca.*
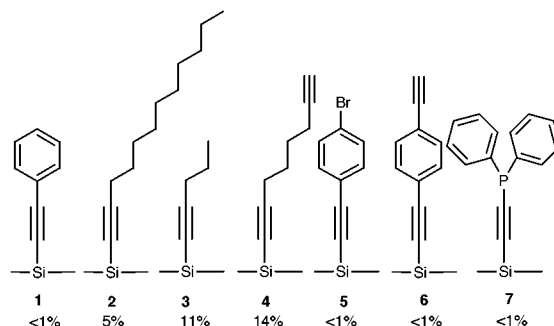
Fig. 2 Representative surfaces prepared by CEG of alkynes to porous silicon. The bold numbers refer to the numbering system in the text, and the % values represent the % photoluminescence (PL) remaining after functionalization through CEG.
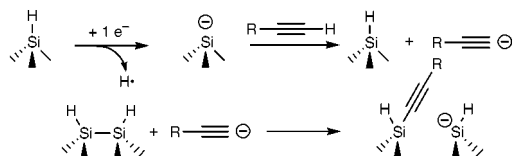
Fig. 3 Proposed mechanism for the CEG of alkynes to porous silicon. Cathodic reduction of a surface Si–H group forms the active silyl anion which initiates the reaction.

20% remaining for the alkyl protected surface **9** as compared to the freshly etched hydride terminated surface.

Stability tests using boiling aqueous NaOH solution (pH 10) demonstrate the chemical resistance of AEG and CEG samples compared to unfunctionalized porous silicon. Unmodified surfaces are destroyed under such conditions in *ca.* 180 s,[3c] whilst the CEG functionalized samples remain essentially unchanged after 10 min except for an increase in the ν(Si–O) mode at 1050 cm^{-1}. Extended treatment with ethanolic HF solution also results in no change in FTIR spectra. The combined stability with respect to both HF and alkaline treatment is known only for Si systems with covalently attached organic layers.[2b–d,11]

We believe the CEG reaction proceeds *via* a silyl anion intermediate formed by reduction of surface Si–H bonds in a space charge layer (Fig. 3) to yield either H$^{\bullet}$ or, 1/2 H$_2$. The silyl anion species has been previously inferred for the mechanism of alkyl halide grafting.[8,12] The subsequent *in situ* generation of a carbanion from deprotonation of the weakly acidic alkyne leads directly to nucleophilic Si–Si bond attack, as observed by previous workers.[5,6,8] The silyl anion is quenched in the presence of a proton source (0.1 M HCl in diethyl ether), leading to no incorporation of alkyne. Other weakly acidic moieties can be grafted *via* this CEG reaction, such as dodecane-1-thiol (surface **10**, Fig. SM11†), presumably through a similar deprotonation step and subsequent attack of Si–Si bonds by an RS$^-$ species. Minor incorporation of butyl groups (2956, 2923 and 2872 cm^{-1}), which may be due to tenacious physisorption or electrochemical decomposition of the NBu$_4$PF$_6$ electrolyte,[13] is observed in all CEG reactions. The butyl groups are not removed after 30 min in boiling chloroform.

Given the observations noted in FTIR of surfaces **8** and **9** (*vide supra*), it is likely that a surface-initiated cationic hydrosilylation mechanism[12,14] is responsible for the Si–C bond formation in AEG reactions (Fig. 4). Positive charges are

stabilized in the depletion layer at the semiconductor–electrolyte interface,[15] which are attacked by alkyne monomers. This can then be the starting point for a successive hydrosilylation or cationic polymerization reaction.[16]

In conclusion, a technique in which alkylation and alkynylation of porous silicon surfaces can be accomplished through CEG and AEG is reported. Future work concerns the further elucidation of the mechanisms *via* investigations using new electrolyte systems and alkynes, and the application of new experimental apparatus.

Notes and references

1 A. G. Cullis, L. T. Canham and P. D. J. Calcott, *J. Appl. Phys.*, 1997, **82**, 909.
2 For reviews of chemistry on porous silicon see the following and references therein: (*a*) *Properties of Porous Silicon*, ed. L. T. Canham, INSPEC, London, 1997; (*b*) M. J. Sailor and E. J. Lee, *Adv. Mater.*, 1997, **9**, 783; (*c*) J. M. Buriak, *Adv. Mater.*, 1999, **11**, 265; (*d*) J. M. Buriak, *Chem. Commun.*, 1999, 1051.
3 (*a*) J. M. Buriak and M. J. Allen, *J. Am. Chem. Soc.*, 1998, **120**, 1339; (*b*) M. P. Stewart and J. M. Buriak, *Angew. Chem., Int. Ed.*, 1998, **37**, 3257; (*c*) J. M. Buriak, M. P. Stewart, T. W. Geders, M. J. Allen, H. C. Choi, J. Smith, D. Raftery and L. T. Canham, *J. Am. Chem. Soc.*, in press.
4 J. E. Bateman, R. D. Eagling, D. R. Worrall, B. R. Horrocks and A. Houlton, *Angew. Chem., Int. Ed.*, 1998, **37**, 2683.
5 (*a*) J. H. Song and M. J. Sailor, *J. Am. Chem. Soc.*, 1998, **120**, 2376; (*b*) J. H. Song and M. J. Sailor, *Inorg. Chem.*, 1999, **38**, 1498.
6 N. Y. Kim and P. E. Laibinis, *J. Am. Chem. Soc.*, 1998, **120**, 4516.
7 C. Vieillard, M. Warntjes, F. Ozanam and J.-N. Chazalviel, *Proc. Electrochem. Soc.*, 1996, **95**, 250; F. Ozanam, C. Vieillard, M. Warntjes, T. Dubois, M. Pauly and J.-N. Chazalviel, *Can. J. Chem. Eng.*, 1998, **76**, 1020.
8 C. Gurtner, A. W. Wun and M. J. Sailor, *Angew. Chem., Int. Ed.*, 1999, **38**, 1966.
9 C. H. de Villeneuve, J. Pinson, M. C. Bernard and P. Allongue, *J. Phys. Chem. B*, 1997, **101**, 2415; C. H. de Villeneuve, J. Pinson, F. Ozanam, J.-N. Chazalviel and P. Allongue, *Mater. Res. Soc. Symp. Proc.*, 1997, **451**, 185.
10 H. C. Brown, *Organic Syntheses via Boranes*, John Wiley and Sons, New York, 1975, p. 100.
11 M. R. Linford, P. Fenter, P. M. Eisenberger and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1995, **117**, 3145.
12 V. V. Jouikov, *Russ. Chem. Rev.*, 1997, **66**, 509; V. Jouikov and G. Salaheev, *Electrochim. Acta*, 1996, **41**, 2623; A. Kunai, O. Ohnishi, T. Sakurai and M. Ishikawa, *Chem. Lett.*, 1995, 1051.
13 C. A. Ferreira, S. Aeiyach, M. Delamar and P. C. Lacaze, *Surf. Interface Anal.*, 1993, **20**, 749.
14 A. A. Khapicheva, N. T. Berberova, E. S. Klimov and O. Yu Okhlobystin, *Zh. Obsch. Khim.*, 1985, **55**, 1533; O. Yu Okhlobystin and N. T. Berberova, *Dokl. Akad. Nauk. SSSR*, 1993, **332**, 599.
15 N. Sato, *Electrochemistry at Metal And Semiconductor Electrodes*, Elsevier, Amsterdam, 1998.
16 *Cationic Polymerization*, ed. R. Faust and T. D. Shaffer, American Chemical Society, Washington DC, 1997, vol. 665.
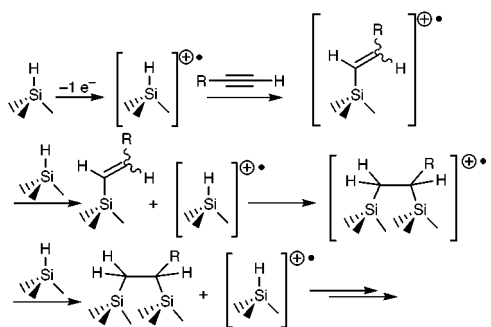
Fig. 4 Proposed mechanism for the AEG of alkynes to porous silicon. Anodic oxidation of a surface Si–H group results in formation of the active cationic silyl species.