Synthesis of ferrocenylphosphine-modified silicon surfaces

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Functional monolayers containing ferrocenylphosphines have been assembled at silicon surfaces by reaction with the hydrogen-terminated layer.

The hydrogen terminated silicon surface formed on etching with aqueous ammonium fluoride or hydrofluoric acid is an integral step in the fabrication of semiconductor devices.[1] Despite the fact that this surface has been very well characterised, it is only comparatively recently that studies examining its functional group reactivity have been reported.[2–9] However, to date, despite the variety of synthetic routes explored, the types of molecules that have been attached to silicon have generally been simple alkyl and aryl groups. The development of chemically-sensitive devices based on silicon requires chemical routes for the covalent attachment of molecules capable of various functions to the semiconductor surface. These may include redox-active molecules, reactive groups and ligands. Towards this end we have previously shown that redox-active monolayers based on ferrocenyl derivatives can be assembled via a two-stage process involving initial formation of a reactive monolayer (terminated with an bromoalkyl headgroup) to which the ferrocenyl group was subsequently attached through alkylation of (dimethylaminomethyl)ferrocene.[6]

We recently reported syntheses of the ferrocenyl(hydroxymethyl)phosphine, $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2P(CH_2OH)_2\}]$ **1** and its oxide, $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2P(O)(CH_2OH)_2\}]$ **2**, and sulfide, $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2P(S)(CH_2OH)_2\}]$ **3**; these derivatives combine a redox centre and ligating donor groups (P, S or O) coupled with a suitable functional group, OH, for attachment to H-terminated silicon surfaces in a single molecule.[10] In this report we demonstrate that covalently attached monolayers incorporating these functionalities can be formed in one step on either porous silicon or single-crystal wafers as a result of the reactivity of the hydrogen terminated silicon surface towards the PCH_2OH group.

A typical procedure for covalent modification involved refluxing a freshly etched piece of (100) oriented Si wafer in a dry acetonitrile solution of the ferrocenyl derivative (0.02–0.07 M, typically 95 mg in 5 ml solvent) for 3 h under nitrogen. Following this reaction, the wafers were washed repeatedly with dichloromethane and dried in a stream of nitrogen. For comparison ferrocenylmethanol-derived monolayers[6] were also prepared, in this case the solvent used was dry hexanes. After monolayer formation ohmic contact was made to the back of the wafers with an In–Ga eutectic and a copper contact wire attached with silver-loaded epoxy. The wafers were then sealed onto glass slides with a silicone rubber such that only the polished face was exposed to solution to enable characterisation by cyclic voltammetry. Fourier-transform IR spectroscopic

characterisation of the monolayers formed on single-crystal wafers was not possible due to the low signal-to-noise ratio. Instead, porous silicon layers were prepared by anodisation of p-Si wafers in HF–EtOH 1:1 electrolyte. After anodisation, the porous silicon was dipped in HF to remove any residual oxide. The high surface area of this material enables simple transmission FTIR characterisation of surface bound species.

Direct evidence for the chemisorption of the ferrocenyl derivatives was obtained from cyclic voltammetric measurements and the results are summarised in Table 1, and Fig. 1 shows typical cases.§ A peak due to oxidation of the surface-
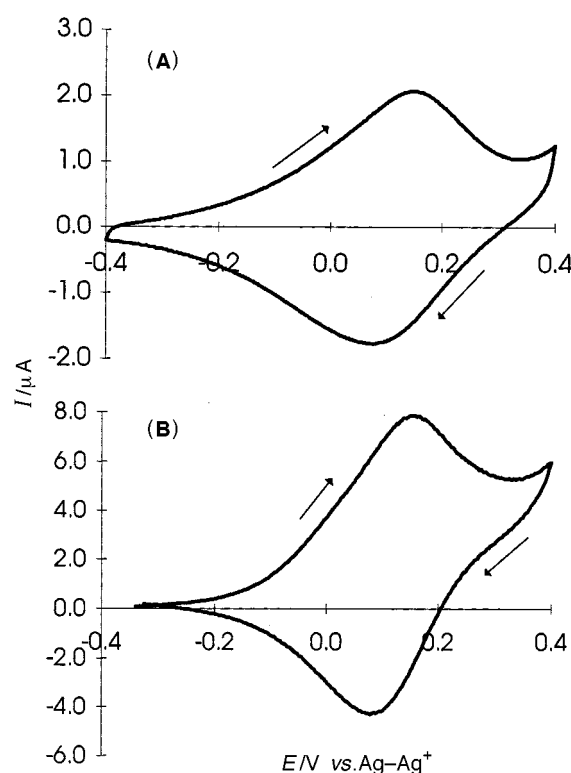

Fig. 1 Cyclic voltammograms of silicon electrodes after derivatisation with (A) ferrocenylmethanol and (B) $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4CH_2P(CH_2OH)_2\}]$ **1**. The scan rate was 100 mV s^{-1}, the reference electrode was Ag–10 mM Ag$^+$ and the electrolyte was 0.1 M NBu$^n_4$PF$_6$. Cyclic voltammograms of **2** and **3** on silicon also showed a reversible wave due to the ferrocene moiety

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§ Cyclic voltammograms were measured in dry MeCN with NBu$^n_4$PF$_6$ as inert electrolyte and a Ag–10 mM AgClO$_4$ reference electrode. All potentials are reported against the ferrocene–ferrocenium couple in acetonitrile solution. The cyclic voltammograms were carried out under ambient illumination to enable reductions to proceed on the p-type material. Boron doped, p-type silicon wafer (10 Ω cm) was obtained from Semimetrics Ltd., UK and cut into pieces ≈1 cm².

Table 1 Electrochemical data for surface attached ferrocenyl derivatives

	Coverage before cycling/10^{-10} mol cm^{-2}	Remainder after 100 cycles (%)	Peak width at half height/mV	$E_s{}^a$/V	$E^{\circ\prime}$ solution^b/V
[Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$CH$_2$OH)]	0.93 ± 0.29	86.3	290	0.031	−0.084
1 [Fe(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$CH$_2$P(CH$_2$OH)$_2$}]	1.19 ± 0.43	24.3	200	0.039	0.023
2 [Fe(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$CH$_2$P(O)(CH$_2$OH)$_2$}]	1.57 ± 0.27	19.8	290	0.106	0.103
3 [Fe(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$CH$_2$P(S)(CH$_2$OH)$_2$}]	1.26 ± 0.46	19.0	350	0.083	0.022

^{a} Mean of anodic and cathodic peak potentials computed from cyclic voltammetry of surface attached ferrocenyl derivatives. ^{b} Formal potential of dissolved species referenced to ferrocene–ferrocenium.
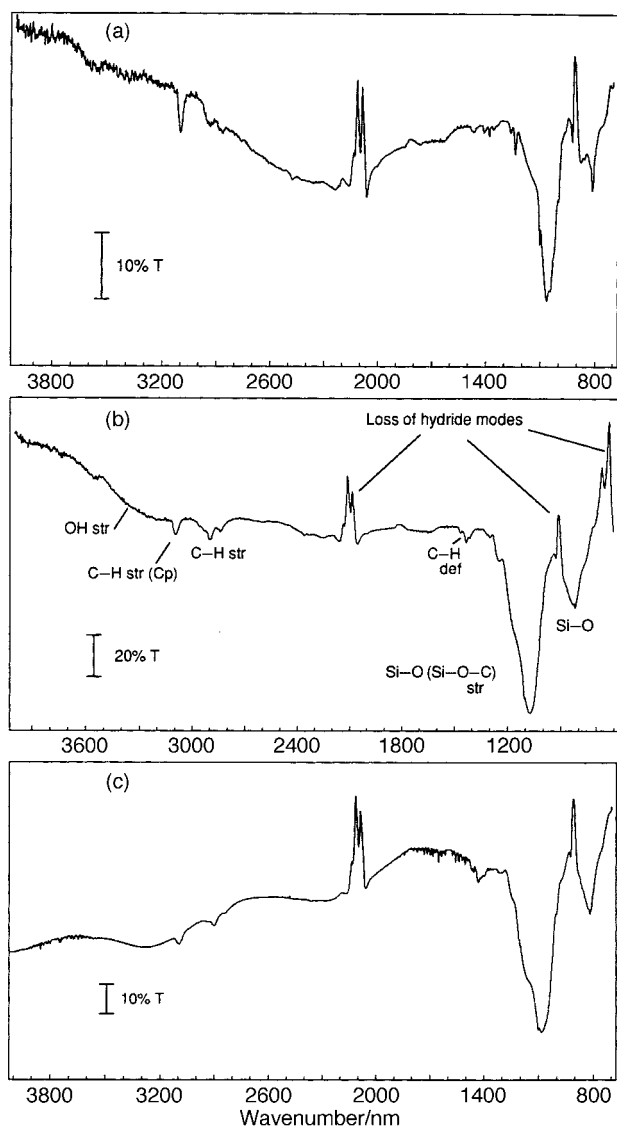

Fig. 2 Fourier-transform IR spectra of (a) ferrocenylmethanol, (b) [Fe(η^5-C$_5$H$_5$){η^5-C$_5$H$_4$CH$_2$P(CH$_2$OH)$_2$}] **1** and (c) [Fe(η^5-C$_5$H$_5$)-{η^5-C$_5$H$_4$CH$_2$P(O)(CH$_2$OH)$_2$}] **2**, on porous silicon. Baseline correction has not been used. Resolution 4 cm^{-1}, with 100 scans per spectrum

bound ferrocenyl residues appears in the cyclic voltammograms partially overlapped with a sloping background due to oxidation of the silicon substrate. The complete irreversibility of silicon oxidation (and of phosphine oxidation in the case of **2**) allows us to obtain the surface coverage of ferrocene accurately from the cathodic peak, on the reverse scan, where the background current is negligible. The diameter of the ferrocenyl group obtained from crystallography is about 0.66 nm[11] and the maximum coverage of ferrocenes on the silicon surface would therefore correspond to 4.4×10^{-10} mol cm^{-2}, assuming a hexagonal close packed arrangement. The mean surface coverages of ferrocenylmethanol and **1**–**3** are comparable (*ca.* 10^{-10} mol

cm^{-2}, Table 1) and in arrangement with previous data for the reaction of molten ferrocenylmethanol with Si(111). These are less though than that observed for the two-step formation of a ferrocenyl monolayer by reaction of (dimethylaminomethyl)-ferrocene with an alkyl bromide terminated monolayer (4.0×10^{-10} mol cm^{-2}).[6] The cathodic peak widths at half height were all greater than the 91 mV expected for a Nernstian surface wave. We have previously observed Nernstian peaks for ferrocenylmethanol monolayers when the surface coverage is a factor of 10 lower. We therefore interpret the broad peaks as evidence for substantial interactions between neighbouring ferrocenyl groups on the surface. As the surface coverages are still less than the value for a close packed monolayer, clustering of the ferrocenes as observed in the gold–ferrocenyl thiol monolayers is therefore indicated.[12]

Despite an anticipated increase in stability for monolayers derived from **1**–**3**, as a result of possible attachment through two hydroxyl groups, these layers are in fact less stable to electrochemical cycling than those derived from ferrocenylmethanol. With continuous cycling the charge passed in the voltammogram decreased (Table 1). Since ferrocenyl monolayers prepared by other routes are quite stable to cycling in acetonitrile solutions and **1**–**3** show reversible cyclic voltammograms in acetonitrile, we suggest that this decrease is not due to chemical irreversibility of the electron transfer but to loss of material from the surface.¶

Infrared spectra of modified porous silicon samples provide evidence for the mode of attachment that is pertinent to the above point. While it was anticipated that **1**–**3** would react with the hydrogen-terminated silicon *via* both OH groups, infrared spectra on porous silicon samples indicated that this is not the case. Fig. 2 shows IR spectra for porous silicon samples derivatised with ferrocenylmethanol, **1** and **2**. Prior to derivatisation porous silicon shows characteristic bands in the infrared due to Si–H$_x$ stretching and bending. On derivatisation these bands were observed to significantly decrease in intensity. In the case of ferrocenylmethanol loss of the O–H stretch is evidence for chemisorption through an Si–O–C linkage. Characteristic bands due to the ferrocenyl moiety are observed, most clearly in the C$_{Cp}$–H stretch at 3100 cm^{-1}. Further bands due to various C–C stretching modes in the cyclopentadienyl groups are evident at 1107 and the 1400 cm^{-1} region. The intense band at 1067 cm^{-1} comprises a number of unresolved modes including the Si–O–C stretch.∥

These features are essentially reproduced in the spectra of **1** and **2** chemisorbed on porous silicon. The characteristic C$_{Cp}$–H stretch at *ca.* 3100 cm^{-1} is evidence of absorption of the ferrocenylphosphines. The expected P=O stretch band in adsorbed **2**, observed in the free molecule at 1127 cm^{-1}, is

¶ The greater loss of **1**–**3** compared to ferrocenylmethanol may be attributed to an increased susceptibility to hydrolysis. Possible explanations for this are (i) accumulation of water at the surface due to the interactions with pendant hydroxyl groups, or (ii) elimination of formaldehyde, a known reaction of the molecular compounds.[13]

∥ Porous silicon has been shown to be extremely susceptible to oxidation on modification.[2,14] A contribution from the Si–O stretch of oxidised porous silicon is therefore expected in this band.

obscured by the broad, intense band due to Si–O–C and Si–O stretching vibrations. However, a significant difference between [Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$CH$_2$OH)] and **1** and **2** is seen with the presence of the broad band at *ca.* 3200 cm^{-1} due to hydrogen-bonded hydroxyl groups. This indicates material either physisorbed or chemisorbed through only one of the alcohol groups in the molecules. Significant physisorption is unlikely as repeated washing in hot chlorobenzene showed no loss of ferrocenylphosphine as determined by IR spectroscopy. In addition, a comparison of the relative integrated intensity of the O–H stretch and the cyclopentadienyl and methylene C–H stretch modes shows that the O–H stretch intensity has decreased by 50% on adsorption compared to the free molecules. These data are consistent with the attachment of ferrocenyl derivatives to the silicon surface *via* one PCH$_2$O–Si link with the second OH group remaining intact.

These results demonstrate that highly functionalised molecules can be attached to single crystal and porous silicon surfaces from solution in a one-step procedure and further extends the range of molecular species chemisorbed through reaction with hydrogen-terminated silicon. However, the apparent lack of stability of the layers to repeated redox cycling highlights the need for alternative synthetic strategies capable of facilitating the attachment of a wide range of functional molecular groups to these surfaces while affording a robust linkage.

Acknowledgements

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