



Electronic structure and band alignment of 9,10-phenanthrenequinone passivated silicon surfaces

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ABSTRACT

In this work we demonstrate that the room-temperature deposition of the organic molecule 9,10-phenanthrenequinone (PQ) reduces the surface defect density of the silicon (100) surface by chemically bonding to the surface dangling bonds. Using various spectroscopic measurements we have investigated the electronic structure and band alignment properties of the PQ/Si interface. The band-bending at the PQ-passivated silicon surface is negligible for both n- and p-type substrates, demonstrating a low density of surface defects. Finally we show that PQ forms a semiconducting wide-bandgap type-I heterojunction with silicon.

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1. Introduction

There is considerable interest in integrating carbon-based organic semiconductors with inorganic semiconductors like silicon [1–3]. While the organic semiconductors can be easily layered with different bandgaps and are potentially low-cost, traditional silicon technology has higher carrier mobilities. Integrating the two to form hybrid organic/silicon interfaces may offer a novel way to improve the device capabilities. For example, a wide-bandgap heterojunction realized using organic/silicon interfaces can reduce parasitic carrier recombination in crystalline silicon solar cells [4], be used to detect gases [5], and enable bio-compatible sensors [6].

Amorphous organic thin films and crystalline silicon surfaces are inherently dissimilar materials, and from an electrical perspective are difficult to integrate. The surface silicon atoms do not chemically react with many classes of organic molecules that might be used to form an organic/silicon interface, and so the silicon valencies can remain unsatisfied. The resulting dangling-bonds lead to mid-bandgap energy-levels at the silicon surface, which degrade device performance by increasing carrier recombination and preventing modulation of the Fermi-level [7].

Recently the electronic passivation of the silicon (100) surface was demonstrated [8] using the organic molecule, 9,10 phenanthrenequinone (PQ) (Fig. 1), which can react with surface silicon atoms by a cycloaddition “redox” process. Minority carrier lifetime measurements yielded surface-state densities of only $\sim 10^{11} \text{ cm}^{-2}$ at the PQ-silicon interface, rivaling the electronic quality of silicon-dioxide passivated surfaces. Further, measurements of metal/insulator/PQ/silicon devices proved that the Fermi level at the PQ-passivated silicon surface is not “pinned” and can be easily modulated over a wide energy range. This is useful for hybrid devices because once the surface is electronically passivated, further organic films can be deposited to tailor the heterojunction energy levels. Furthermore, the π -conjugated aromatic structure of PQ imparts semiconducting properties, so the PQ layer can act as a non-insulating bridge between the crystalline and amorphous layers, enabling high electronic-quality organic/silicon heterojunctions [4].

In this paper, we investigate the electronic properties of the PQ/silicon interface using various spectroscopic techniques. X-ray Photoelectron Spectroscopy (XPS) is used to probe the bonding between PQ and the silicon surface. XPS is also used to detect the presence of any acceptor or donor-like surface defects by measuring the band-bending at both n- and p-type PQ-passivated silicon surfaces. Ultra-violet and inverse photoelectron spectroscopy (UPS, IPES) are used to investigate band alignment at the PQ-silicon interface for both p- and n-type silicon, which is important to understand charge transport properties of the interface. From these measurements we infer that the interface is remarkably “ideal”; free from interface defects and Fermi-level pinning.

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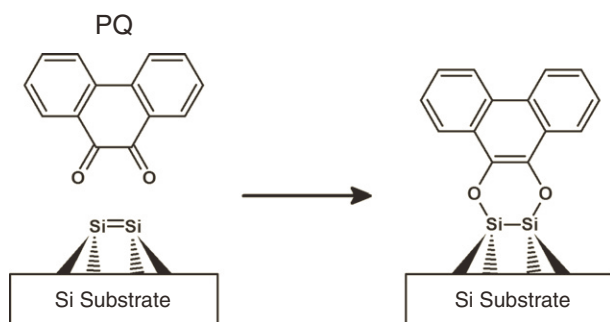


Fig. 1. The reaction between 9,10-Phenanthrenequinone (PQ), the surface passivation precursor, and silicon as proposed by Fang et al. [9]. Note that a phenolic-like product is obtained.

2. Materials and methods

PQ was purchased from Sigma Aldrich (99% purity) and used as is. Prior to passivation by PQ, the silicon (100) wafers were first cleaned by rinsing with acetone, methanol and 2-propanol in an ultrasonic bath for 10 min each. Next, trace metal contaminants were removed by the standard RCA method [10]. Lastly, the wafers were dipped in a 1:100 aqueous hydrofluoric acid solution for 1 min to strip any oxide layer. The resulting hydrogen-passivated Si wafers were loaded into the vacuum chamber, with a base pressure of $<6 \times 10^{-7}$ mbar, for PQ deposition. Inside the chamber, the silicon surface was exposed to ~ 30 Langmuirs (1 Langmuir = 1.3×10^{-6} mbar s) of thermally evaporated PQ vapor, to give an estimated thickness of 10 nm. The thickness was estimated using a quartz crystal microbalance which was pre-calibrated by measuring thicker PQ films (50 nm) with a surface profilometer. All spectroscopic analysis was done in a separate ultra-high vacuum (UHV) chamber (base pressure $<2 \times 10^{-10}$ mbar). During transport to the UHV chamber, test samples were exposed to air for no more than 5 min.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy (XPS)

Under certain high temperature annealing conditions, the silicon (100) surface undergoes a $[2 \times 1]$ reconstruction to form rows of silicon “dimers” [11]. Each dimer consists of a Si-Si bond, with strong σ and weak π character [11,12]. This gives the dimer a chemical behavior analogous to that of a C—C double bond, and it can participate in a $[4 + 2]$ cycloaddition (Diels–Alder-like reaction) with conjugated dienes [13]. A similar heteroatomic $[4 + 2]$ cycloaddition reaction was previously suggested between the carbonyl carbons (C O) of PQ and the silicon dimers on the silicon (100) surface (Fig. 1) [9]. In this reaction the Si atoms are formally oxidized, and the PQ is formally reduced to a 9,10-dihydroxyphenanthrene adduct.

Our process does not use a high temperature anneal prior to PQ deposition. Hence we do not expect a $[2 \times 1]$ reconstructed surface. Instead we expect an ill-defined hydrogen-passivated silicon (100) surface. To investigate the bonding between this surface and PQ, we measured the XPS spectra of the C 1s and Si 2p core levels using the Al K α line (1486.6 eV). The C 1s spectrum of a PQ-passivated p-type silicon ($<0.005 \Omega \text{ cm}$), shown in Fig. 2 (solid line), can be decomposed into two components (dash-dot curves). The first peak at 284.7 eV is usually a signature of simple aromatic carbon atoms and can be attributed to the peripheral aromatic rings of PQ [9]. However, the binding energy of the second peak at 286.2 eV, is significantly lower than the 287.7–289.3 eV range typically associated with carbonyl group carbon atoms [9] and is in the range reported for typical phenolic carbons [14]. The shift in the binding energy of this second

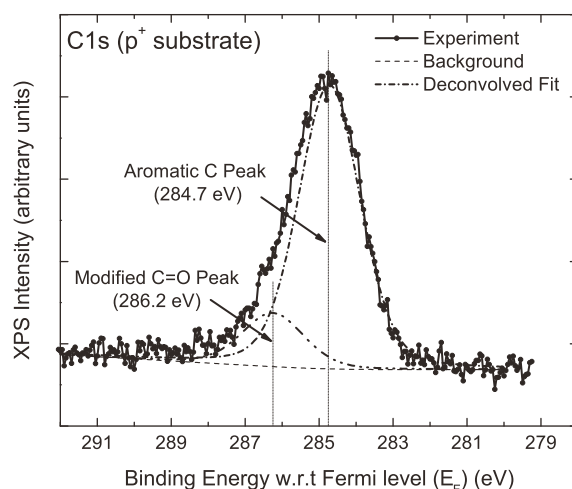


Fig. 2. C 1s XPS spectrum for PQ-passivated highly-doped p-type silicon (100) surfaces. The data (black line) can be further resolved into 2 distinct peaks (dash-dot) at 284.7 eV and 286.2 eV. These peaks correspond to the binding energies of the aromatic C (C C) and the phenolic-like (C O) species of the bound PQ molecule, supporting the mechanism proposed in Fig. 1.

peak indicates that while the aromatic rings are intact, the carbonyl groups of PQ at the PQ/Si interface have been strongly modified by interacting with the underlying silicon surface. There are 12 aromatic and 2 carbonyl carbon atoms in the starting PQ molecule, so the aromatic carbon signal is expected to be six times ($12/2$) stronger than the carbonyl carbon signal. This compares well with the measured signal strength ratio (the area under the peaks) of 5.2:1 of the Si-bound species. All these results are congruent with the proposed cycloaddition mechanism where the silicon atoms react exclusively with carbonyl groups of PQ (Fig. 1b) making them more phenoxy-like.

While the exact structure of the underlying silicon surface is not known, any unreacted silicon valencies (“dangling” bonds) may lead to midgap defect states at the silicon surface. These states may carry charge, causing the bands at the surface to bend towards midgap. The amount of this surface band-bending (ΔE_{BB}) can be inferred from the position of the Si 2p peak in the XPS spectrum using the technique developed by Kraut et al. [15]. Note that the probing depth of XPS is large enough to allow measurement of the substrate Si 2p core level through the 10 nm thick PQ layer [16]. Also the bulk of the Si 2p signal comes from the top few Si layers (4–6 layers corresponding to a depth of ~ 2 – 3 nm), where the band bending is basically the same (± 10 – 20 meV) as at the very surface of the Si substrate.

We have previously measured the Si 2p peak to be 98.9 ± 0.1 eV below the Fermi level (E_F) for a highly-doped p-type silicon wafers (p^+ , doping $> 10^{19} \text{ cm}^{-3}$), known to have flat bands at the surface ($\Delta E_{BB} = 0$). Similar values of Si 2p binding energy have been reported previously [17]. In comparison, for a p^+ wafer that was cleaned and hydrogen-passivated as described above (but not PQ-passivated), the Si 2p peak was measured at 99.4 ± 0.1 eV below the Fermi level (Fig. 2, top curve). This corresponds to a downward surface band-bending of 0.5 eV, presumably due to a large density of positively charged donor-like surface defects ($\Delta E_{BB} = 0.5$ eV). The presence of such defects at the hydrogen-passivated surface is not unexpected, as the “imperfection” of a wet-cleaned silicon (100) surface has been previously reported [10,18].

PQ deposition reduces the amount of band-bending. A highly-doped p-type wafer onto which PQ was deposited, as per the method described above, shows the Si 2p peak at 99.1 ± 0.1 eV with respect to E_F (Fig. 2, middle curve), corresponding to a band-bending of only 0.2 ± 0.1 eV. ($\Delta E_{BB} = 0.2$ eV). This 0.3 eV decrease of ΔE_{BB} is especially significant because the bands of heavily-doped silicon are very

difficult to bend. The fact that the Fermi-level is pinned at midgap on a highly doped wafer, indicates that the defect density is still high at the hydrogen-passivated surfaces. PQ-deposition substantially reduces the defect density, allowing the Fermi level at the surface to get closer to the band edge. This is consistent with the proposed mechanism (Fig. 1), according to which PQ reacts with and consumes the “dangling” bonds on the silicon surface.

The component corresponding to the Si-O bonding is not readily apparent in the Si 2p core level, even though Si-O bond is presumably present in PQ-passivated silicon as per the proposed mechanism (Fig. 1). There are two reasons for this lack of evidence. First, the shift in the Si 2p level expected for a Si chemically bonded to three silicon atoms and one oxygen is only ~ 0.5 eV [19]. This shift is too small for the resolution of the XPS measurements performed in this work. Second, the intensity of the shifted component is expected to be small compared to the intensity of the unshifted Si core level. This is because only two Si atoms per PQ molecule contribute to the shifted signal, while the unshifted signal has contributions from many layers of subsurface Si atoms.

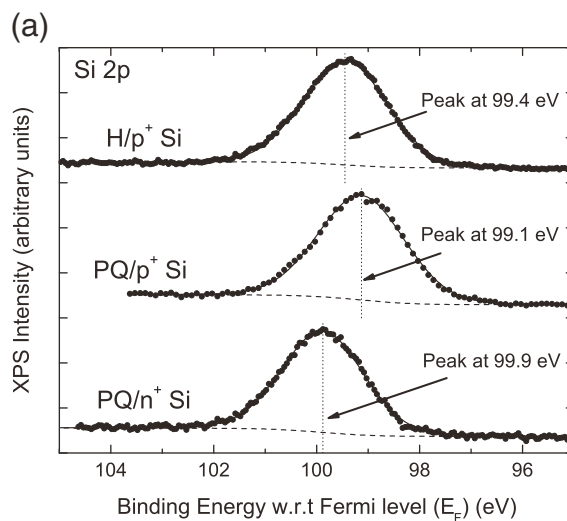
Though the lower band-bending suggests a reduction of the number of charged defects, the presence of neutral defects is still possible. For example, there might still be a high density of midgap acceptors that are neutral above the Fermi level and hence do not cause band-bending on a p-type surface. To investigate this possibility, similar measurements were also done on highly-doped n-type (n^+) surfaces. For PQ-passivated n^+ wafers (Fig. 3a, bottom curve) the Si 2p binding energy was 99.9 ± 0.1 eV. The expected difference in Fermi level positions on p^+ and n^+ Si is 1.12 eV, so in the flat band condition the n-type surface Si 2p core level should have a binding energy of 100.0 ± 0.1 eV. Comparing the two numbers, we estimate the surface band-bending on the PQ-passivated n^+ surfaces to be $0.1 \text{ eV} \pm 0.1 \text{ eV}$ ($\Delta E_{BB} = 0.1 \text{ eV}$). The difference in Si 2p binding energies between the p^+ and n^+ silicon surfaces ($99.9 - 99.1 = 0.8 \text{ eV}$) is the range of surface energies over which the Fermi-level may be modulated. These measurements agree with our previous results, which reported that at PQ-Si interfaces surface recombination velocities are low ($\sim 150 \text{ cm/s}$), and the Fermi level can be modulated from accumulation to inversion by application of an electric field [8].

3.2. Ultra-violet and inverse photoelectron spectroscopy

A distinct advantage of using PQ-passivation over traditional passivating layers like silicon-dioxide, which is an insulator, is the possibility for current-conduction across the PQ/silicon interface. The conjugated π bonds of PQ suggest that it is a semiconducting molecule and hence it can transport charge more efficiently. For a more thorough evaluation of the electrical conduction properties of PQ, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were determined by UPS and IPES. Together with the XPS results, these techniques provide an accurate determination of the alignment between the PQ and Si energy levels at the interface. Measurements were taken on both highly-doped p- and n-type silicon surfaces.

The UPS measurements used the He I line (21.22 eV) of a gas discharge source, and IPES used a commercial electron gun and a fixed photon energy detector (centered at 9.2 eV), the details of which have been published elsewhere [20]. The resolution of the UPS and IPES measurements was estimated at 0.15 and 0.45 eV, respectively. The energy scales of the UPS and IPES spectra were aligned by measuring the position of the Fermi edge with both techniques on freshly evaporated Au films.

The UPS and IPES spectra for a PQ layer on p^+ Si are shown in Fig. 4. In the UPS spectrum, the signal at the lowest binding energy corresponds to the electrons photoemitted from the top of the filled states at the surface [21]. Due to the thickness of the PQ overlayer (10 nm) the signal from the Si valence band is assumed to be entirely



(b)

	$E_{2p} - E_F$ (eV)	ΔE_{BB} (eV)
Flat-band p^+ -Si	98.9 ± 0.1	0.0
H/ p^+ -Si	99.4 ± 0.1	0.5
PQ/ p^+ -Si	99.1 ± 0.1	0.2
Flat-band n^+ -Si ^a	100.0 ± 0.1	0.0
PQ/ n^+ -Si	99.9 ± 0.1	-0.1

^a p^+ -Si at flatband + 1.1 eV

Fig. 3. (a) Si 2p binding energies (E_{2p}), w.r.t to bulk Fermi level (E_F), of highly-doped silicon (100) surfaces. The three curves represent solution-processed H-passivated p-type surface (H/ p^+ -Si), PQ-passivated p-type surface (PQ/ p^+ -Si), and PQ-passivated n-type surface (PQ/ n^+ -Si). (b) The surface band-bending (ΔE_{BB}) in silicon for the three cases.

suppressed. Thus the edge closest to zero gives the HOMO edge of the bound PQ molecule on the passivated p^+ Si at 1.2 eV below the Fermi level. Similarly, in the IPES spectrum, the signal at the lowest binding energy corresponds to the bottom of the empty states, i.e. the edge of bound PQ LUMO [21]. On PQ-passivated p^+ Si, the LUMO edge is at 2.0 eV above the Fermi level. Hence, the HOMO-LUMO difference, i.e. the energy gap, of PQ is 3.2 eV.

The UPS signal at the highest binding energies (labeled as onset in Fig. 4a) corresponds to the photoemission cut-off from which vacuum level and the work function (Φ) are extracted [21]. For the PQ-passivated p^+ Si, $\Phi = 4.1 \text{ eV}$. Based on these results, the ionization energy (IE) and electron affinity (χ) of PQ-passivated p^+ Si can be determined to be 5.3 eV and 2.1 eV, respectively. These numbers are consistent with a first-principles calculations reported in Ref. [22]. Typically, for a 10^{19} cm^{-3} doped p-type silicon with negligible band-bending, the work-function, the ionization energy and the electron affinity are of the order of 5.2, 5.2 eV and 4.0 eV, respectively. Together with the -0.2 eV band-bending in Si (calculated by XPS as described above), we can calculate the band alignment at the PQ/Si interface. Overall, the PQ- p^+ Si interface is a type-I heterojunction, as detailed in Fig. 5a.

Using PQ-passivated silicon, we had previously demonstrated an n-channel field-effect transistor (FET), where surface passivation and gate insulator deposition were done at low-temperatures ($<100^\circ \text{C}$) [8]. Unlike in a conventional FET, the silicon surface in

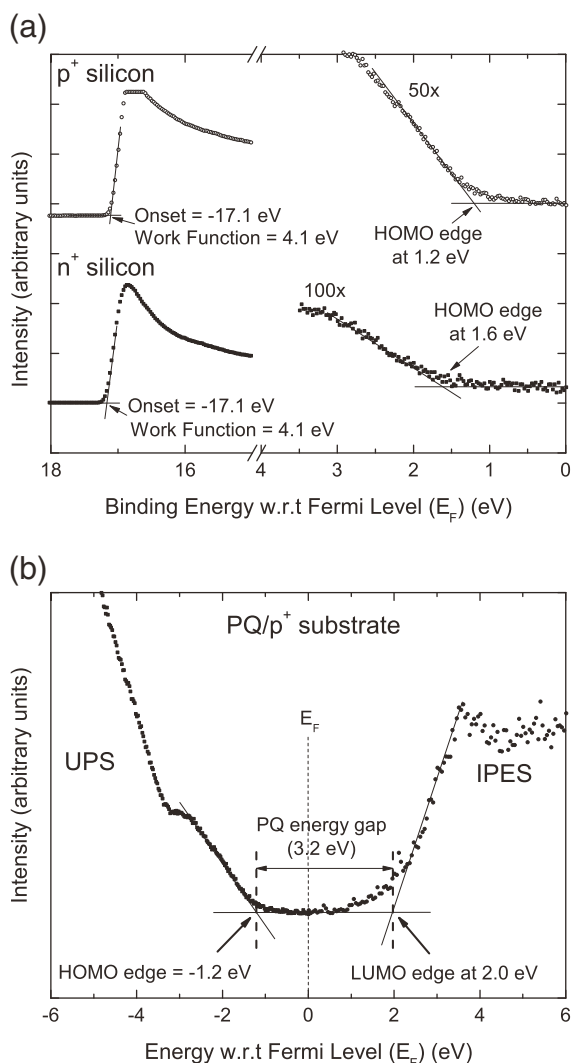


Fig. 4. (a) He I (21.22 eV) UPS spectra of a PQ-passivated highly-doped p- and n-type silicon (100) surfaces. Onset of HOMO edge in p⁺ Si can be seen more clearly in Fig. 3. (b) Composite UPS and IPES of a PQ-passivated highly-doped p-type silicon (100) surface. The resulting band-diagram is shown in Fig. 5.

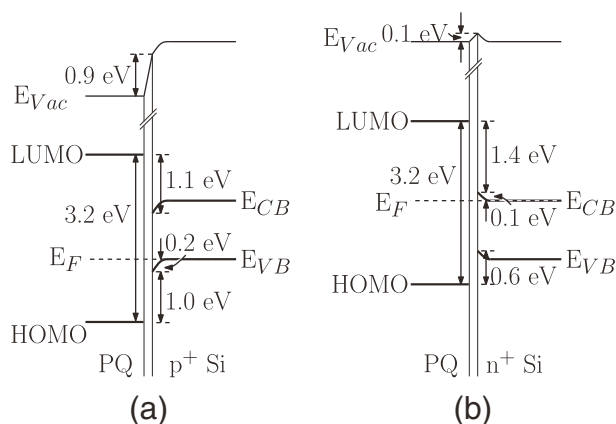


Fig. 5. Band offsets at the PQ/Si Interface: The band diagram of the PQ-passivated silicon surface for highly doped (a) p-type and (b) n-type silicon (100) surfaces. The band-bending in silicon is extracted from the XPS data (Fig. 3a). The offsets at PQ/Si heterojunction have been extracted from the UPS and IPES data (Fig. 4a, b). In both cases and interface dipole is measured.

these devices was not passivated by a high-quality silicon oxide layer, instead PQ was used to passivate the silicon dangling-bonds to form a gate-metal/insulator/PQ/Si type of structure. Electron mobilities greater than $600 \text{ cm}^2\text{V}^{-1} \text{ s}^{-1}$, comparable to high-quality oxide-passivated FETs, were measured on these devices. Such high mobilities allowed us to assert that (a) the PQ/Silicon interface is of very high electronic quality, i.e. interface defect density is low and (b) the electrons in the inversion layer are localized in silicon and not PQ. While (a) simply follows from the results of band-bending measurements, reasons for (b) merit more discussion. If we are to assume, for the sake of argument, that the inversion-layer electrons are localized in the organic PQ, and not Si, the expected mobilities would be far lower and more in line with mobilities of organic FETs (typically $<10 \text{ cm}^2\text{V}^{-1} \text{ s}^{-1}$) [23,24]. The fact that we see mobilities that are 2 orders of magnitude higher and comparable to crystalline Si FETs, strongly suggests that this is not that case. The band-alignment data of Fig. 5a provides the precise explanation. In an n-channel FET, the bands of p-Si bend down under positive gate-bias to form a thin layer of mobile electron in Si (the “inversion” layer) at the insulator/Si interface. However, the electron-barrier at the PQ/p-Si interface, between the conduction band (CB) minimum of Si and the LUMO of PQ, is quite significant (1.1 eV). In PQ-passivated Si, the inversion layer electrons are blocked by this barrier from getting into the PQ layer.

An interesting, but not well understood, observation is the presence of an interface dipole at the PQ/p⁺-Si interface. It can be quite large, equal to 0.9 eV for p⁺ and 0.1 for n⁺ Si, and depends on the Si work function. The presence of interface dipoles at organic/silicon interfaces that depend on the work-function of the underlying substrates, have been previously observed for a number of metal/organic interfaces [25,26], and a number of mechanisms have been proposed to explain their origin [27]; for example charge transfer between the chemisorbed organic and underlying metal [26]. The origin of the dipole at the PQ/silicon interface, and its dependence on silicon doping (or equivalently, the silicon work function), could be similar. A more detailed analysis of the phenomenon is the object of ongoing study.

4. Conclusion

We have demonstrated that the organic molecules PQ chemically bond to the silicon (100) surface atoms, and in the process consume the “dangling” bonds typically found on bare Si surfaces. Band-bending is greatly reduced at both n and p-type silicon surfaces. This implies low densities of both acceptor and donor-like defects at the interface. The PQ/Si interface is not insulating, rather the alignment of the energy levels is such that PQ forms a wide-bandgap type-I heterojunction with silicon. These results are promising and could provide a way to integrate organic materials with silicon to form hybrid organic/silicon electronic devices.

Acknowledgments

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