Silicon surface passivation by an organic overlayer of 9,10-phenanthrenequinone

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Merged organic-silicon heterojunction devices require the passivation of dangling bonds at the silicon surface, preferably with a low-temperature process. In this paper, we demonstrate the high-quality passivation of the silicon (100) surface using an organic molecule (9,10-phenanthrenequinone, PQ). PQ reacts with the dangling bonds, thus providing a bridge between organic semiconductors and silicon. We measure low recombination velocities (~150 cm/s) at the PQ-silicon interface. Metal/organic-insulator/silicon capacitors and transistors prove that at PQ-silicon interface, the Fermi level can be modulated. The formation of an inversion layer with electron mobility of 600 $cm^2/V{\cdot}s$ further demonstrates the passivation quality of PQ.
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There is considerable interest in integrating organic and silicon-based semiconductor devices.[1–3] Organic-semiconductor/silicon interfaces can provide a route toward wide band gap heterojunctions for solar cells,[4,5] while organic-insulator/silicon interfaces may be useful for crystalline silicon thin-film transistors[6] (TFTs). However, such devices are fundamentally limited by the large number of defect states introduced by the dangling bonds on the silicon surface. The defect states substantially increase the recombination of minority carriers, undesirably bend the bands at the surface, and may pin the Fermi level preventing the modulation of surface carrier densities. To reduce the surface defect density, layers of insulators like silicon dioxide are traditionally deposited/grown at high temperatures (600–1000 °C). Not only are such temperatures too high for organic layers but for current to flow across the heterojunction, the passivating layer should be semiconducting and not an insulator.

Previous work on the surface chemistry of silicon suggested that the organic molecule, 9,10-phenanthrenequinone [PQ, Fig. 1(a)], reacts with the dangling bonds on the [2×1] reconstructed silicon (100) surface via a heteroatomic Diels–Alder reaction[7] [Fig. 1(b)]. Also interesting is the fact that π-electron conjugation of PQ, and hence its semiconducting property, is maintained in the reaction. In this paper we conclusively demonstrate, using minority carrier lifetime and device measurements, that a layer of PQ deposited at room temperature reduces the surface defect density, i.e., electrically passivates the silicon(100) surface.

All the PQ depositions were done in a vacuum chamber with base pressure of 6×10^{-7} mbar, by exposing silicon wafers to 20–30 Langmuirs of thermally evaporated PQ (1 Langmuir=1.3×10^{-6} mbar s). Prior to the deposition, silicon wafers were thoroughly cleaned by the standard RCA method and hydrogen-terminated by dipping in dilute hydrofluoric acid (1:100) for 1 min.

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Dangling bonds at the silicon surface are well-known to cause mid gap defect states that act as minority carrier recombination centers. Moreover, the electrical charges at these defects can bend the bands toward the midgap, which attracts even more minority carriers to the surface, exponentially increasing recombination.[8] The rate of recombination, characterized by the recombination lifetime, can be experimentally measured by photoconductance decay.[9] In this technique, excess carriers are generated in silicon with a pulse of light and the lifetime is extracted from the decay rate of the minority carriers as their density falls back to equilibrium.[10] Recombination lifetimes were measured, at an estimated average minority carrier density of 10^{15} cm^{-3}, for a $15-\Omega\cdot$cm p-type boron-doped silicon (100) wafer with three different surface treatments: oxide, native-oxide, and PQ-passivated.[11] With a coating of "gate-oxide"-quality silicon dioxide, grown at 1050 °C in oxygen, a lifetime of 107 μs ("oxide") was measured (Table I). Next, the oxide at

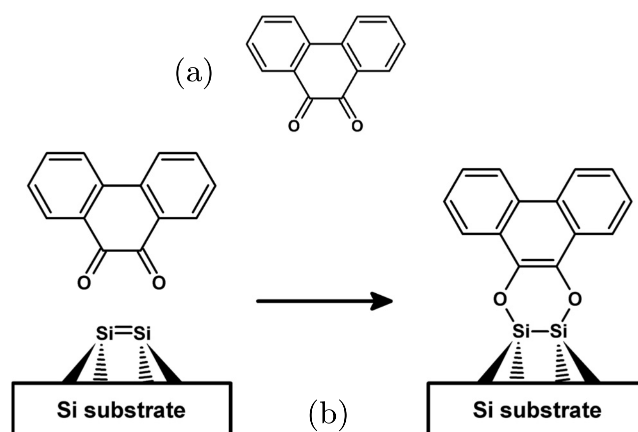

FIG. 1. (a) PQ. (b) The proposed reaction between PQ and silicon (100) dimmer (Ref. 7). The reaction consumes the dangling bonds while preserving the aromatic π-conjugation of PQ. This reduces the surface defect density, allowing the formation of electrically passivated but conducting organic-silicon interfaces.

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TABLE I. The calculated minority carrier recombination lifetimes in silicon at average minority carrier density of 10^{15} cm^{-3} and extracted SRV for both p and n-type substrates. The three conditions represent different surface treatments; passivated with a high-quality thermal oxide, unpassivated (native oxide), and PQ-passivated.

	Effective lifetime (μs)			SRV (cm/s)		
	Oxide	Native oxide	PQ-passivated	Oxide	Native oxide	PQ-passivated
p-type	107	12	78	9	4990	142
n-type	192	26	122	23	2040	130

the top surface was etched away and a native oxide was allowed to form on the exposed silicon surface. The native oxide-silicon interface is known to have a very high defect density, and hence the lifetime dropped to 12 μs ("native-oxide"). Finally, after etching away the native oxide, PQ was deposited on the bare silicon surface and the measured lifetime recovered to 78 μs ("PQ-passivated"). Similar results were also obtained for a $3-\Omega\cdot$cm phosphorus-doped silicon wafer. In both cases, the lifetimes of PQ-passivated and thermal-oxide-coated wafers are comparable, demonstrating the passivation quality of PQ.

For a quantitative estimation of the surface defect density, the lifetime data was further analyzed. Minority carriers can recombine either at the bulk or at the surface defects, and experimentally an "effective" recombination rate is measured. The "effective" lifetime (τ_{eff}) relates to the two recombination mechanisms, characterized by the bulk (τ_{bulk}) and surface (τ_{surf}) lifetimes as follows:[12]

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surf}}. \tag{1}$$

We can assume that τ_{bulk} remains unchanged for all the three surface treatments, since PQ is deposited at low temperatures (<100 °C). Hence, any change in τ_{eff} is exclusively due to differences in τ_{surf}, which is directly affected by the surface defect density. One can estimate τ_{bulk}, and hence extract τ_{surf} for the three passivation conditions, using the generalized quasisteady-state analysis.[13]

Surface recombination is also sometimes described in terms of the surface recombination velocity (SRV, s). Assuming negligible band-bending, the SRV for each of the three surface treatments can be calculated from τ_{surf}. Thermal silicon-dioxide/silicon interfaces have low defect density,[14] and hence very low SRV, <30 cm/s, were extracted for both type of substrates. For the PQ-passivated p-type and n-type wafers recombination velocities of 142 cm/s and 130 cm/s, respectively, were calculated (Table I). The low surface recombination rates for both electrons and holes proves that at the PQ-silicon interface not only is the defect density very low but the bands are essentially flat. This also justifies the assumption of negligible band-bending used above to calculate these velocities. In contrast, at the native silicon surfaces, SRV of 4990 cm/s and 2040 cm/s are calculated for p and n-type substrates, respectively. In general, the relationship between SRV and the surface defect density (N_T) is quite complicated[15] but in its simplest form

$$s = v_{th}\sigma N_T, \tag{2}$$

where v_{th} is the carrier thermal velocity and σ is the defect capture cross-section.[12] Assuming a thermal velocity of 10^7 cm/s and a capture cross-section of $\sim 10^{-16}$ cm^2, we estimate the defect density to be roughly 10^{11} cm^{-2} for PQ-passivated surfaces; i.e., only 1 in 10 000 silicon surface atoms is unpassivated.

To demonstrate the ability to modulate the Fermi level at the PQ-silicon interface, we fabricate metal/insulator/semiconductor capacitors on PQ-passivated silicon wafers. The structure consists of lightly doped p-type substrate coated with layers of an insulating polymer resin (AZ5214) and aluminum (Al) [Fig. 2(a)]. The resin is selected as the insulator due to its low-temperature deposition (vacuum bake at 95 °C) and lack of any aggressive chemistry with silicon or PQ. For comparison, a control structure without the PQ passivation was also fabricated. The C-V characteristics of these two structures, measured at a frequency of 1 MHz and a dc-bias step rate of ~ 0.25 V/s, are shown in Fig. 2(b). Without PQ the capacitance is fixed, presumably due to the large density of defects which make it impossible to bend bands at the silicon surface. On the other hand with PQ, the measured characteristic is typical of a metal/insulator/semiconductor system: the larger flat capacitance at negative voltages denoting accumulation, and the decreasing capacitance at positive voltages denoting depletion (and possibly inversion).

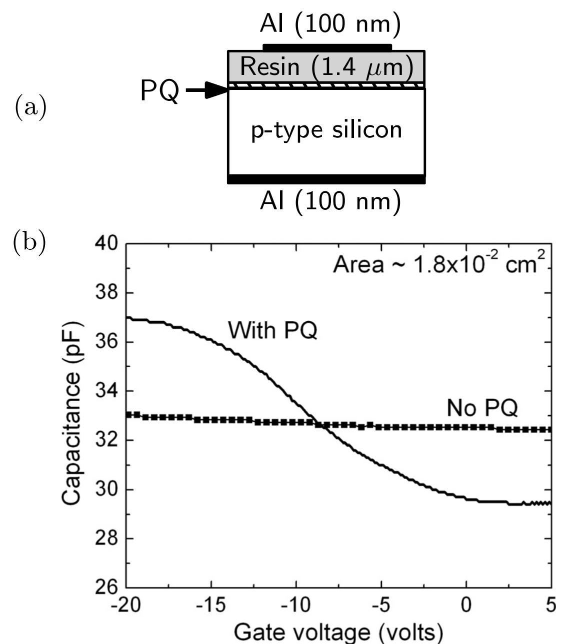

FIG. 2. (a) PQ-passivated metal-insulator-semiconductor capacitor structure. The insulator is AZ5124 polymer resin. (b) The small-signal capacitance (1 MHz) of a metal-insulator-semiconductor capacitor on p-type silicon.

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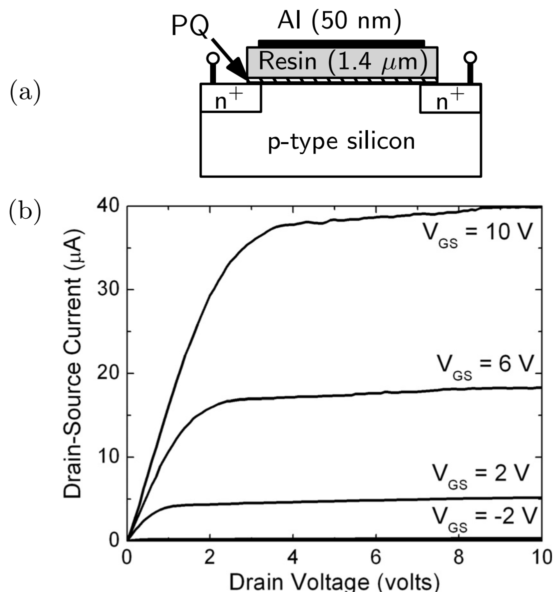

FIG. 3. (a) The n-channel MISFET device structure. The L and W of the devices are ~1 mm and ~1.91 mm, respectively. (b) Drain current vs drain voltage characteristics at different gate voltages (V_{GS}).

While the clear presence of the two regions confirms that at the PQ-passivated surface the Fermi level can be modulated, a flat capacitance at positive gate voltages alone does not conclusively prove inversion. The characteristics would be very similar if a large density of acceptor-like defect states were pinning the Fermi level before actual inversion is reached.[16] To test for true inversion, we fabricate n-channel metal-insulator-semiconductor field-effect transistor (FET) (MISFET) devices with a PQ/insulator stack on light-doped p-type substrates [Fig. 3(a)]. The source and drain are formed by phosphorous ion implantation and annealing, before the deposition of either PQ or the organic insulator. Well-behaved n-channel MISFET characteristics are observed which convincingly show an "inversion" layer of mobile electrons [Fig. 3(b)]. A peak electron field-effect mobility of ~640 $cm^2/V\ s$ is extracted from the drain current versus gate voltage characteristic at a drain voltage of 0.1 V. The mobility is four times higher than what was previously reported for crystalline silicon FET with an organic gate dielectric,[6] and is similar to our control device with a thermally-grown silicon dioxide as the insulator. These results prove that at the PQ-silicon interface Fermi level can indeed be modulated from midgap to the conduction band edge.

Other groups have also attempted to passivate the silicon surface with organic materials, notably with alkyl chains derivatives.[2,3] Our work differs in several critical aspects. First, a high degree of electronic passivation, approaching that of silicon dioxide, has been achieved by depositing an organic molecule. Second, alkyl chains are inherently insulating, while PQ maintains aromaticity after bonding to the silicon surface. This would enable charge transport across the organic-silicon interface, which is important for devices such solar cells and bipolar transistors. Third, while most of the previous work has focused on the Si (111) surface, we demonstrate passivation of the silicon (100) surface, which is more commonly used in conventional silicon technology. PQ was selected for this study due to its unique chemical properties[7] and easy commercial availability. One might expect that with a systematic approach and tailored molecules even better organic-silicon interfaces can be achieved.

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