

# REDUCTION OF MINORITY CARRIER RECOMBINATION AT SILICON SURFACES AND CONTACTS USING ORGANIC HETEROJUNCTIONS

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## ABSTRACT

We present an approach for silicon (100) surface passivation using the organic small molecule, 1-10 phenanthrenequinone. Lifetime measurements show that on passivated silicon surfaces, recombination velocities of less than 100 cm/s can be achieved. Such electrically inactive surfaces are used to demonstrate a wide-bandgap organic/silicon heterojunction which reduces the effective minority carrier surface recombination at the metal/silicon contact compared to a similar structure without the organic layer.

## INTRODUCTION

With steadily decreasing cell thicknesses and improving substrate bulk lifetimes, minority carrier recombination at the surface and metal contacts is becoming increasingly important; especially in cells with high bulk lifetimes [1].

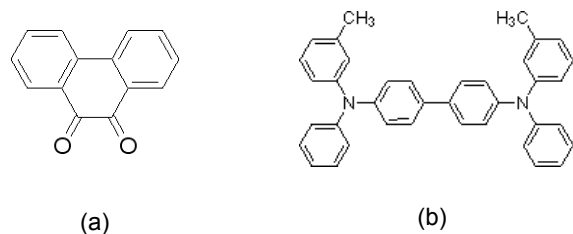
In silicon solar cells, front and back surface fields are used to reduce the recombination at metal contacts. These surface fields can be induced by a high-low junction ( $p^+/p$  or  $n^+/n$ ), field effect of a gate or through a floating  $p/n$  junction [2]. Recombination can also be reduced by using barrier of a wide-bandgap heterojunction. GaAs concentrator solar cells which use the heterojunction barrier (with AlGaAs as the wide-bandgap semiconductor) report higher efficiencies than cells with homojunction BSFs [3]. Unfortunately there is no wide-bandgap crystalline semiconductor that can be epitaxially grown on silicon.

Recently, HIT solar cells [4] were demonstrated which used a PECVD grown amorphous-Si/crystalline-Si heterojunction for solar cell application. In these devices the amorphous silicon was the wide-bandgap semiconductor but it also satisfied another important criterion; it provided excellent passivation for the surface of the crystalline silicon. The authors reported an effective SRV of < 100 cm/s.

As an alternative to a-Si, organic semiconductors could in principle also be used to realize a wide-bandgap heterojunction silicon contact. With large band offsets (>1 eV) and hence the possibility of even more reduction in recombination, an organic/silicon heterojunction could theoretically have even higher efficiencies than current

solar cells. The critical issue in this approach would also be the silicon surface passivation.

In this work, we demonstrate a) a new passivation method for silicon (100) surface and b) an approach that combines PQ passivation and an organic semiconductor to create an organic/silicon heterojunction that reduces the minority carrier recombination at the metal/p-type Si contact. Surface recombination velocities (SRV) under 100 cm/s were measured in 1, 10-phenanthrenequinone (PQ: Fig. 1(a)) passivated n and p-type silicon substrates. The wide-bandgap organic semiconductor used is N,N'-diphenyl-N,N'-bis(3-methyl-phenyl)-1,1'-biphenyl-4,4'-diamine (TPD: Fig. 1(b)), an organic semiconductor with a bandgap of 3.08 eV (LUMO=2.29 eV and HOMO= 5.37 eV) [5].



**Fig. 1 (a)** Molecular structure of PQ, the surface passivation precursor.

**(b)** Molecular structure of TPD, the wide-bandgap organic used as the electron barrier for organic/silicon heterojunction.

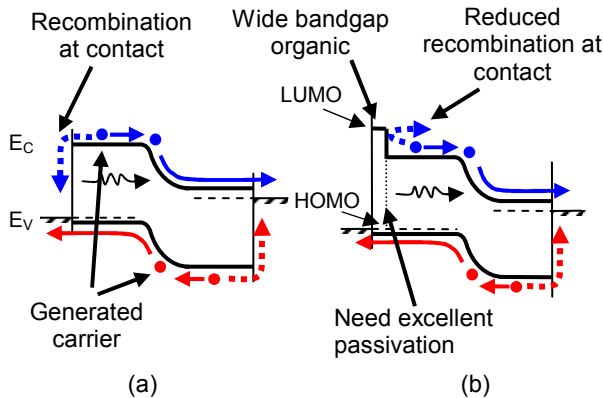
## APPROACH

Solar cells are diodes optimized for absorbing light and separating the generated carriers. The open circuit voltage ( $V_{OC}$ ) and short circuit current ( $J_{SC}$ ), the figures of merit for solar cells, are related by the following equation:

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_0}\right) \quad (1)$$

where,  $J_0$  is saturation current density of the diode

With the short circuit current ( $J_{sc}$ ) already near its theoretical maximum, the only way to further increase  $V_{OC}$



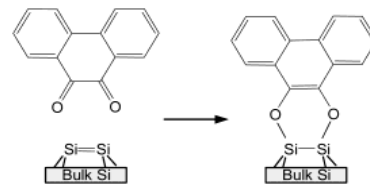
**Fig. 2** (a) Band Diagram of solar cell in which recombination at the metal contact dominates. The solid lines are desired direction of generated carrier flow and the dashed line represents the loss mechanism. (b) Effect of a suitable heterojunction that reduces the electron recombination at the anode due to the offset in the conduction band. A complementary structure would reduce the hole recombination at the cathode.

and hence increase efficiency, is to decrease  $J_0$ . The  $J_0$  of the solar cell is a direct measure of minority carrier recombination in the device at a fixed bias voltage. By reducing recombination we reduce the  $J_0$ .

In solar cells with high lifetime and thin substrates recombination happens largely at surfaces and the metal-silicon contacts (Fig. 2(a)). In principle one could reduce this recombination by using a heterojunction as shown in Fig.2 (b), where a wide bandgap semiconductor is used to reduce the electron recombination at the anode. The bands are chosen such that there is a large offset at the conduction band to repel the carriers but almost no offset at the valence band to keep the series resistance low.

Organic small molecules with conjugated  $\pi$ -electron systems are known to be semiconductors [6]. The bandgap between the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) is typically larger ( $\sim 2-3$  eV) than that of crystalline silicon. These organic semiconductors are often non-crystalline and their deposition does not require a direct lattice match.

However, the heterojunction would reduce recombination only if the silicon surface is well passivated. The bare silicon surface has dangling bonds which cause midgap states. These states would allow minority carriers to recombine at the organic/silicon interface, neutralizing any positive effect of the band offset. Methods that use dielectrics to passivate the silicon surface, like oxide or nitride, are not useful due to their high series resistance to the majority carrier flow required for the device operation. Chemical treatments like a hydrofluoric acid dip [7], which passivates the dangling



**Fig. 3.** The reaction between PQ and silicon dimer as proposed by Fang *et al.* [9].

bonds with hydrogen, and alcoholic iodine [8] are not stable. Thus there is a need for passivation technique without these limitations.

We demonstrate the passivation of the silicon surface using an organic small molecule; 1,10-phenanthrenequinone (PQ: Fig. 1(a)). The molecule is semiconducting and compatible with low cost thermal deposition. Fang *et al.* previously studied the bonding of this molecule on silicon surfaces [9]. Based on spectra and microscopy data, they proposed a heteroatomic Diels-Alder reaction between PQ and the silicon dimer on the silicon (100) surface (Fig.3). In the scheme, PQ chemically bonds to the silicon surface while maintaining its  $\pi$ -electron conjugation; which is important for efficient charge transfer across the organic/silicon interface.

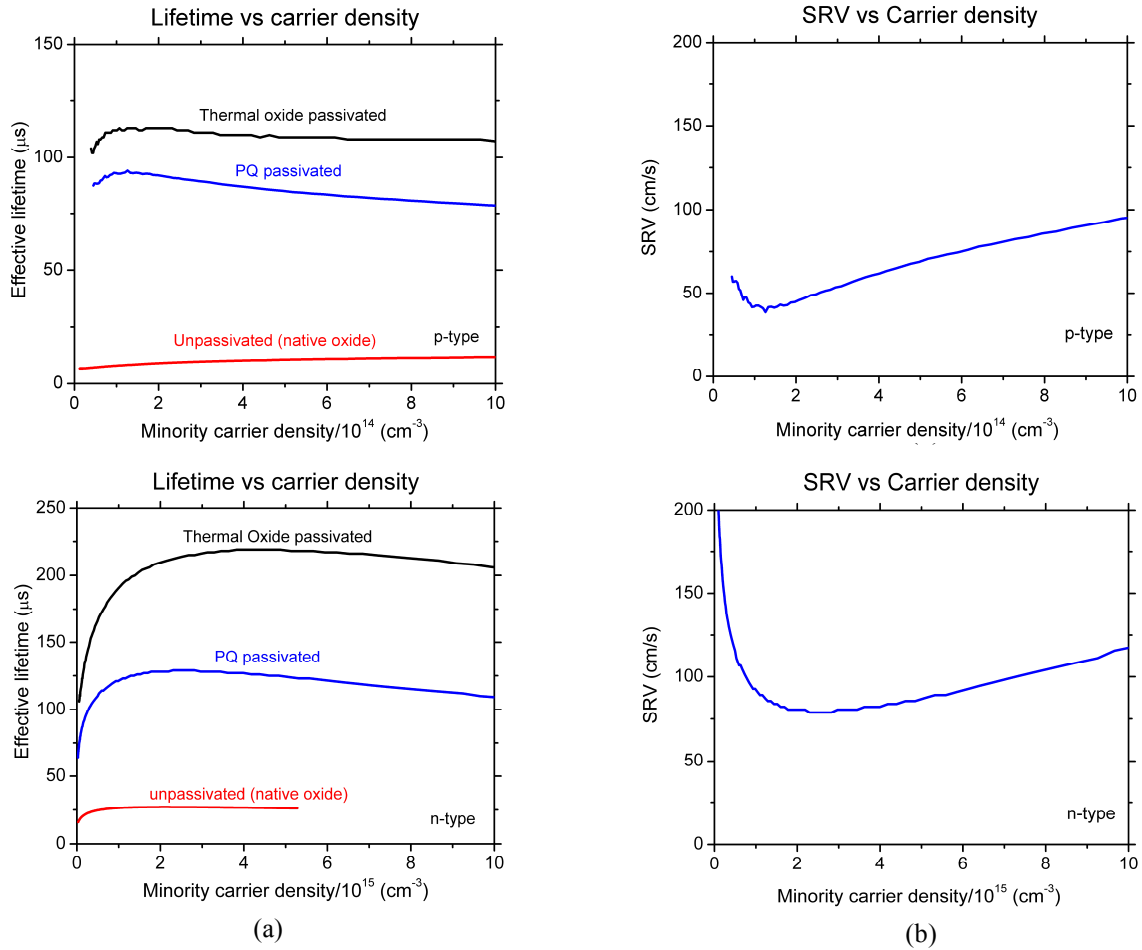
Previously, various groups have worked on organic-silicon hybrid solar cells [10-12]. In these cells, the organic semiconductors were used to form the junction (hence, the electric field) that separated the generated carriers. Our approach however is fundamentally different. We begin with a p-n junction in silicon. The organic layer in our structure is instead used to reduce the minority carrier recombination at the metal/silicon contact.

## EXPERIMENTS

### Deposition

Prior to all PQ depositions silicon (100) wafers were cleaned in trichloroethylene, acetone, methanol and isopropanol for 10min each in an ultrasonic bath. This was followed by immersion in  $H_2O_2:H_2SO_4$  (1:4) at  $80^\circ C$  and then dilute HF ( $\sim 1:100$ ). The samples were then put in a DI  $H_2O:H_2O_2:H_2SO_4$  (1:1:5) solution at  $70^\circ C$ . Finally a DI  $H_2O:HF$  (1:100) dip was done strip the chemical oxide and yield a clean hydrogen passivated surface. The samples were quickly loaded into the deposition chamber .

All organic depositions were done by thermal evaporation in a system with base pressure of  $<2 \times 10^{-7}$  torr. Deposition rates were kept low at  $\sim 0.02$  nm/s. In all the experiments mentioned in this paper, a  $\sim 10$ -nm thick layer of PQ was deposited. The thickness was monitored by a profilometer calibrated quartz crystal. After deposition the sample was left in the chamber for several hours to insure that the reaction between PQ and silicon reaches completion.



**Fig. 4 (a)** Effective lifetime vs. minority carrier density for p and n type silicon wafers. Samples are coated with either with the thermally grown oxide(control), PQ, or nothing (unpassivated). **(b)** Extracted surface recombination velocity vs. minority carrier density for p and n type samples passivated with PQ.

### Surface recombination velocity measurement on passive n and p-type surfaces.

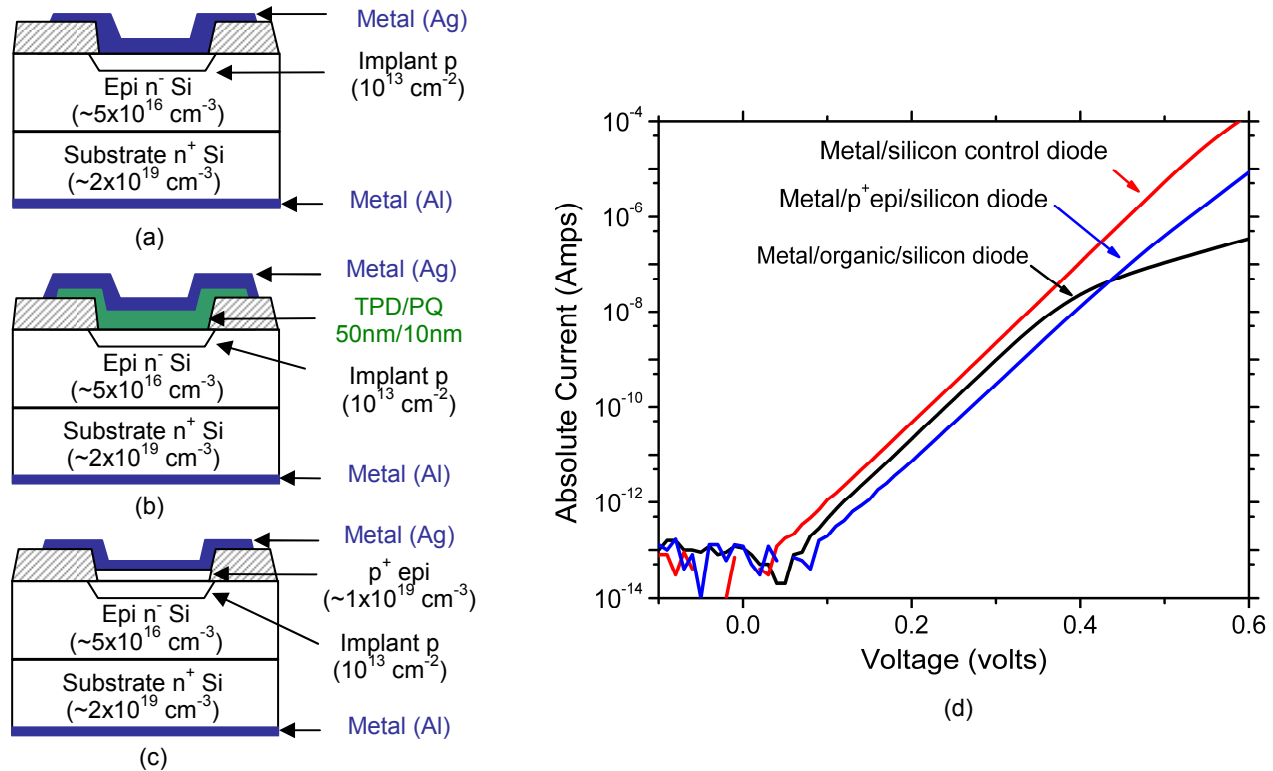
To test the passivation quality of the organic layers, lifetime measurements were performed using WCT-100, a contactless lifetime meter manufactured by Sinton Consulting. The system uses quasi-steady-state photoconductance (QSSPC) method to calculate effective lifetime as a function of minority carrier density. For a sample of thickness  $d$ , with bulk lifetime of  $\tau_B$ , minority carrier diffusion coefficient of  $D$  and surface recombination velocity on one of the side be  $s$  and the other 0, the effective lifetime measured will be [13]:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_B} + \beta^2 D \quad (2)$$

$$\text{where, } \tan\left(\frac{\beta d}{2}\right) = \frac{s}{\beta D} \quad (3)$$

Given the bulk and effective lifetime the recombination velocity,  $s$ , of a sample can be calculated. The test samples were lightly doped CZ wafers with a dry 1050 °C thermal oxide. First the lifetime of oxide-covered samples was measured. As shown in Fig. 4(a), we obtained lifetime of ~100 μs and ~200 μs for p (10 Ohm-cm) and n (3 Ohm-cm) type oxide covered wafers respectively. Assuming the SRV at Si-SiO<sub>2</sub> interface is negligible; the lifetime measurement gives a good approximation of the bulk lifetime (using Eq. 2 & 3). A 2.5-cm hole was then etched into the top oxide to expose bare silicon surface. Native oxide was allowed to form on the surface and lifetime was measured for the second time (labeled “unpassivated (native oxide)” in Fig. 4). Finally PQ was deposited as per the recipe described above and lifetime measured a third time.

From the data we can extract the SRV at the interface as a function of minority carrier density (Fig. 4(b)). In the best case for the PQ passivated wafers, SRV of 68 cm/s and 90 cm/s were obtained at densities of  $5 \times 10^{14} \text{ cm}^{-3}$  and  $5 \times 10^{15} \text{ cm}^{-3}$  for p and n-type samples, respectively.. Assuming a capture cross-section of the surface defects



**Fig. 5 (a)** Metal-silicon diode structure. **(b)** Organic heterojunction diode structure. **(c)** p<sup>+</sup> epi-silicon diode structure. **(d)** IV characteristics of the 200µm x 200µm test structures clearly showing a decrease in recombination currents with the organic blocking layer.

to be  $\sim 10^{-16}$  cm<sup>2</sup> and thermal velocity of  $\sim 10^7$  cm/s, the calculated density of electrically active surface defects is  $\sim 10^{11}$  cm<sup>-2</sup>. For comparison, for the unpassivated wafer the SRV was 5600 and 1200 cm/s in p and n-type wafers, respectively.

#### Reduced minority carrier recombination at the p-type silicon-metal contact

Organic/silicon heterojunctions were fabricated to test for reduced recombination at the metal/silicon contacts.

Doping profiles in the structure were carefully designed to make the electron current (from n<sup>+</sup> to p silicon) exceed the hole current (from p to n<sup>+</sup> silicon) by at least a factor of 10. The shallow p-type implant ensures that the dominant contribution to electron current is the recombination occurring at the metal/silicon contact. Therefore, if the minority carrier current is indeed reduced by the heterojunction we would expect to see a clear decrease in total current compared to a control structure.

High quality n-type ( $\sim 10^{16}$  cm<sup>-3</sup>) silicon layers were first epitaxially grown on highly doped (<0.005 Ohm-cm) CZ Si (100) substrates. The thickness of the layers was  $\sim 6\mu\text{m}$ . The wafers were oxidized in steam at 1050 °C to form a thick (750 nm) oxide into which 200-µm-sided square

holes were photo-lithographically etched; these defined the devices. The subsequent boron implant (p-type) was done at 50 keV with a dosage of 10<sup>13</sup> cm<sup>-2</sup>. The samples were then annealed at 900 °C for 20 min.

Devices from the same batch were processed in three different ways (Fig 5): a) metal-silicon diode, b) organic/silicon heterojunction diode, and c) epitaxially grown p<sup>+</sup>-silicon homojunction diode. The metal-silicon diode is the control structure. The organic/silicon heterojunction diodes were fabricated by deposition of the PQ passivating layer followed by the 50nm of TPD. For the p<sup>+</sup> epi-silicon diodes, a thin (200nm) highly doped silicon layer ( $\sim 10^{19}$  cm<sup>-3</sup>) was selectively grown before depositing the top metal.

The I-V characteristic of these structures is shown in the Fig 5(d). The current of the p<sup>+</sup> epi-silicon diodes are 10x lower than the control structure. This was expected due to the back surface field effect of the highly doped layer, which would reduce the recombination at the contact. This confirms that the total device current is dominated by electron injection into the top p-type region. The organic/silicon heterojunction diode shows a 2x reduction in current as compared to the control structure, with no step above room temperature, after the silicon processing.

This result demonstrates that organic/silicon heterojunctions are a promising new way to reduce the minority carrier recombination at the metal/silicon contacts. More work is still needed to reduce the series resistance, optimize the band offsets and understand the interaction of metal on the silicon and organic surfaces.

### CONCLUSION

We have demonstrated excellent passivation by an organic, 1-10 Phenanthrenequinone, on both n and p-type silicon (100) surfaces. Calculated from lifetime measurements of PQ passivated silicon, surface recombination velocities of <100 cm/s were achieved. To the best of our knowledge, this is the first time an organic/silicon interface with such good electrical quality has been reported.

Using the passivation scheme we also show a reduction of minority carrier recombination at p-type metal-silicon contact using TPD/PQ-Si heterointerface..

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