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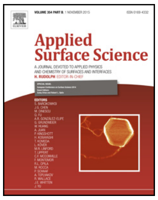

Examining the free radical bonding mechanism of benzoquinone– and hydroquinone–methanol passivation of silicon surfaces

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ABSTRACT

The surface passivation of p-benzoquinone (BQ) and hydroquinone (HQ) when dissolved in methanol (ME) has been examined through effective lifetime testing of crystalline silicon (c-Si) wafers treated with the aforementioned solutions. Changes in the availability of both photons and protons in the solutions were demonstrated to affect the level of passivation achieved. The requirement of both excess protons and ambient light exposure to maintain high effective lifetimes supports the presence of a free radical species that drives the surface passivation. Surface analysis suggests a 1:1 ratio of HQ-like bonds to methoxy bonds on the c-Si surface after treatment with a BQ/ME solution.

1. Introduction

Crystalline silicon (c-Si) is a dominant material in photovoltaic (PV) devices, and the treatment of wafer surfaces to reduce detrimental surface recombination effects is critical to c-Si-based device performance. To date, the predominant methods for surface passivation require processes that elevate the system temperature for material deposition. Room temperature solution-based methods, however, provides a rapid, less-intensive means to electrically passivate c-Si surfaces. The molecular mixture quinhydrone (QHY), which is a 1:1 mixture of p-benzoquinone (BQ) and hydroquinone (HQ), as shown in Fig. 1, has been demonstrated to passivate c-Si surfaces, and solutions of QHY constituents in methanol (ME) that have been examined in order to more fully understand the bonding mechanisms involved [1]. If the mechanisms underlying this high-lifetime passivation method can be determined, the information can be used to engineer materials that will provide the same functionality for the c-Si surface, but with other, device-specific functions. The capability to combine c-Si surface passivation with specified electrical properties, such as electron or hole blocking, high carrier mobility, or transparency to a specific wavelength range has a direct bearing on the growing field of hybrid organic–inorganic PV devices, or any device system considering the implementation of alternative engineered materials.

While much work has been performed to demonstrate the efficacy of QHY/ME solutions, the mechanisms behind the high-quality passivation and the degradation of the effect once the passivated c-Si sample is removed from solution are still unknown [2–9]. Work on separate solutions of the constituent species of QHY has shown BQ/ME outperforms HQ/ME, but that HQ/ME passivated surfaces will improve given more than 3 h of exposure to solution [6,10]. These studies use effective lifetime to monitor and evaluate the performance of the passivants.

Surface analysis has also been performed using Fourier transform infrared spectroscopy (FTIR). These studies indicate that surfaces treated with QHY/ME, BQ/ME, and HQ/ME all display Si-methoxy and Si—HQ bond vibrations, with little if any noticeable Si—O bonds present [10]. Due to the Si surface termination with HQ-like molecules, it has been suggested that BQ converts into the free radical QH• through the abstraction of a H, and it is this free radical that bonds to a Si dangling bond [10,11]. For HQ solutions, it is proposed that HQ first converts to BQ, an already demonstrated process [10,12–14].

In this work, the existence of the proposed free radical QH• in this particular passivation system will be examined through effective lifetime measurements of solution passivated c-Si. The

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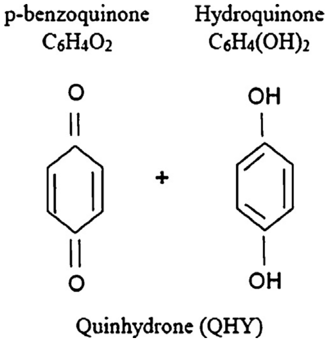

Fig. 1. Constituent molecules of the quinhydrone compound.

importance of protons and photons to the passivation mechanism – necessary components in the conversion process of QH• – will be demonstrated. The surface chemistry of c-Si after passivation with BQ/ME will also be examined in order to support the QH• hypothesis, and to determine the ratio of organic molecules present.

2. Experimental

The metric used for determining the effectiveness of surface passivation is effective lifetime (τ_{eff}), which is measured by contactless photoconductance decay (PCD) using a WCT-120 from Sinton Consulting, Inc., with upgraded hardware to measure high resistivity wafers [15,16]. General mode was used, which combines quasi-steady-state and transient measurement analysis for more flexible data collection. Due to the contactless nature of the measurement, τ_{eff} could be measured while the Si wafer was still in the passivating solution. An optical constant of 0.7 corresponding to wafer thicknesses between 100 and 400 μm thick with no coating on the surface was used for the generalized analysis [17].

Two wafer types were tested with the following specifications: (1) n-type, P-doped, ⟨1 0 0⟩, double-side polished (DSP), 500 μm thick, 20–30 Ω-cm, 2″×2″, and (2) p-type, B-doped, ⟨1 0 0⟩, DSP, 525 μm, 10 kΩ-cm, and 2″×2″.

Wafer preparation included a surface clean, hydrogen termination, and organic surface passivation. The wafers were cleaned using a three-step process: 5 min in 4:1 Piranha at approximately 100 °C, 5 min in DI H_2O, and 2 min in dilute HF at 1:50 HF:DI H_2O.

After cleaning, the wafers were immediately immersed into the appropriate passivation solution that had been mixed in a clear, acid-proof bag with a zip closure. The use of a bag, rather than a dish, allows for accurate lifetime measurements without the need for system recalibration. The solutions were prepared with a methanol (ME) (J.T. Baker CMOS Grade, as-is) solvent, unless otherwise noted. The organic molecules p-benzoquinone (BQ) (98+% Alfa Aesar, as-is) and hydroquinone (HQ) (99% Acros Organics, as-is) were used as the passivants, and were mixed with the ME to produce 0.1 M solutions of BQ/ME and HQ/ME, respectively.

Lifetime measurements began with $t = 0$ indicating the first measurement taken immediately after wafer immersion into the passivation solution. The effective lifetime was measured and recorded every 15 min, unless otherwise noted, for a period of 2–24 h, depending upon the sample, and the wafer remained immersed in solution for the duration of the experiment. The measured photoconductance is only that of the wafer, as the solution has a negligible photoconductance. The length of time over which effective lifetime was measured will be noted where applicable. Unless otherwise noted, τ_{eff} is reported at a minority carrier density of $1e15\,\text{cm}^{-3}$.

Varied lighting conditions were implemented in order to observe the effects of light on the passivation reaction. A light-proof enclosure was built around the tester, providing the ability to eliminate ambient light from some experiments and expose the wafer to light only during the brief flash for carrier excitation. The following lighting conditions were examined:

(1) *Full light* – The entire measurement preparation process was performed in full ambient laboratory light conditions.
(2) *Partial light* – The passivation solution was prepared in full ambient laboratory light conditions. After cleaning and H-termination of the surfaces, the c-Si wafer was immersed into the passivation solution in an environment absent of light. The PCD measurements were taken in a light-proof enclosure, and the sample remained in said enclosure for the full duration of the experiment (2–24 h). The solution and immersed wafer were exposed to light only during the illuminating flash for each measurement.
(3) *No light* – The passivation solution was mixed in the absence of light, followed by wafer immersion, also in the absence of light. The PCD measurements were taken in a light-proof enclosure, and the sample remained in said enclosure for the full duration of the experiment (2–24 h). Again, the solution and immersed wafer were exposed to light only during the illuminating flash for each measurement.

In order to evaluate the relative magnitude of the light dose from the PCD flash when compared with ambient light, a Sekonic L-358 light meter was used to determine the lux of the light sources. To calculate the final dose from each source, the lux was multiplied by the duration of the exposure over a 1 h timeframe. The result is that the PCD flash accounts for 2% of the total light dose when compared with the ambient light dose over a 1 h period.

A PHI model 5600 laboratory X-ray photoelectron spectrometer (XPS) equipped with AlKα mono source was used to survey the deeper core states. Analysis was taken at a base pressure of 8×10^{-10} Torr, where each region was taken at a pass energy of 23.50 eV with 0.2 eV/step at a spot size of 800 μm at a collection angle of 45°. All fittings were done with a PHI Matlab code version V3.0. This program used the general forms of the Gaussian–Lorentzian sum (GLS) for the peak fitting.

3. Results and discussion

3.1. Active bonding constituent and time effects in QHY/ME solutions

For QHY/ME passivation, literature suggests that BQ is the active passivant, and that the passivation effects of HQ improve over prolonged exposure of the wafer to the solution [6,10]. This is confirmed under full light conditions on both n- and p-type wafers, using a clean Si wafer immersed in ME as a control sample.

As can be seen in Fig. 2, the BQ/ME solution provides an immediate, high lifetime passivation. The HQ/ME solution does not have the same immediate effect as BQ/ME, performing only slightly better than the control solution within the first 2 h of wafer immersion. At 24 and 48 h, however, the lifetimes of n-type samples passivated with HQ/ME greatly improve, indicating an increased passivation capability over time.

In order to further evaluate the change in passivation capability of HQ/ME over time, p- and n-type wafers were immersed in HQ/ME, and lifetimes were measured every 15 min under full light conditions for a duration of 14 h (n-type) to 20 h (p-type) – the period of time required for the lifetime to reach asymptotic behavior. The changes in lifetime as a function of time for wafer immersion are shown in Fig. 3(a) and (b) for n- and p-type wafers, respectively.