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Analysis of silicon wafer surface preparation for heterojunction solar cells using X-ray photoelectron spectroscopy and effective minority carrier lifetime



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ABSTRACT

We report a systematic study on the optimal conditions for silicon surface preparation to ensure excellent passivation at the crystalline-amorphous silicon (c-Si/a-Si:H) interface of silicon heterojunction solar cells for both untextured and chemically textured samples. X-ray photoelectron spectroscopy (XPS) was utilized to analyse the elemental composition of known silicon impurities on the wafer surface. Surface purity and passivation quality, characterized by effective minority carrier life time (τ_{eff}) and implied open circuit voltage (iV_{oc}), were estimated using either quinhydrone-methanol solution or 10 nm intrinsic a-Si:H layers deposited using DC plasma process. This study confirms that surface damage etch (SDE), tetra-methyl ammonium hydroxide (TMAH) texturing and the subsequent TMAH residue removal are the most critical steps in the cleaning process, supporting a simplified wafer cleaning approach that is concise, repeatable and uses minimal volume of chemicals.

1. Introduction

With steady and continuous improvements in the record efficiencies of silicon heterojunctions (SHJ) solar cells [1,2], greater attention has been placed on optimizing specific aspects of the SHJ cell fabrication. A wide range of research efforts that cut across surface characterization [3], passivation [4], doped layer optimization [5], surface texturing [6,7], metallization [8], and design [9] have been directed towards improving SHJ cell efficiencies. Each of these optimization techniques improves the optical and/or electrical performance of the cell. However, the purity of the silicon wafer surface on which the cell is fabricated has a primary effect on the performance of the cell irrespective of the optical and/or electrical optimization achieved. SHJ cells, unlike conventional cells made from diffused junctions, have their junctions formed by growing thin-doped and intrinsic layers on the silicon surface. Thus, the a-Si:H/c-Si interface is an integral part of the junction, which places great emphasis on the purity of the wafer surface. Excellent surface passivation is contingent on a well-prepared surface free from organic contaminants, particles and metallic ions, thereby reducing surface recombination and enabling very high open circuit voltage (V_{OC}) necessary for achieving high efficiency devices. A very aggressive and complex cleaning regime could be devised to yield a high purity surface, while also producing excess chemical waste, introducing variability from run to run, and undermining repeatability. Due to the critical nature of the c-Si wafer surface property, and the key role it plays in the overall SHJ cell performance, we detail here a comprehensive study of different common wafer surface preparation steps, analysing their relative significance in ensuring an optimal cell performance. Common challenges with standard wafer cleaning procedures like variability and complexity are also highlighted in this work.

To effectively carry out this study, the wafer surface was characterized at different stages during the cleaning process in order to quantify the impact and value of each step. Treated wafer surfaces were characterized using x-ray photoelectron spectroscopy (XPS) for elemental analysis. Of the various surface characterization techniques available, XPS was utilized because of its ability to detect electrons originating from the top few atomic layers, making it a unique surface sensitive technique for elemental analysis. The result from the XPS analysis of each cleaning step was then compared with effective minority carrier lifetime (τ_{eff}) and implied open circuit voltage (iV_{OC}),

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estimated using Sinton Quasi-steady-state photo-conductance (QSSPC) decay measurement [10] on samples passivated with quinhydronemethanol solution [11]. Quinhydrone-methanol was utilized in this study because it presents a quick and effective chemical surface passivation method for measuring the lifetime of Si wafers, with comparable passivation as a-Si:H layers. Surface passivation was repeated with a 10 nm intrinsic a-Si:H layer deposited on both sides of wafers using a previously validated deposition recipe, to verify the efficacy of each cleaning process for solar cell fabrication. QSSPC decay measurement from both quinhydrone-methanol and 10 nm intrinsic a-Si:H layer corroborates the XPS data and supports a simplified wafer cleaning approach.

2. Experimental details

In this study, we show results from qualitative and quantitative surface analysis of 140 µm chemically polished n-type Cz monocrystalline silicon wafers with (100) orientation and $4-5 \Omega$ -cm resistivity. Wafers were cut and processed as 25×25 mm square samples. Multiple samples were treated to unique wafer-cleaning sequences for reproducibility and effectiveness. ACS certified chemicals were supplied from Fisher Chemical except Quinhydrone (Aldrich Chemistry) and Ammonium hydroxide (J. T Baker) and were used as received for this study. Initially the effects of surface damage etch (SDE), wafer degreasing, and metal ion removal were verified. SDE was carried out using potassium hydroxide (KOH). KOH, an anisotropic etchant of silicon, etches the {110}, {100} and {111} planes at a ratio of 400:200:1 at 85 °C [12]. Each side of the Si wafer was etched by about 3 µm in a 20% wt. aqueous KOH solution in this study, leaving behind K⁺ ions on the wafer. Seidel et al. summarized the overall gross reaction of KOH with silicon as [13]:

$$Si + 2OH^{-} + 2H_2O \rightarrow SiO_2(OH)_2^{2-} + 2H_{2(g)}$$
 (1)

Removal of dust particles and wafer degreasing were performed using one of three methods: 1) pressurized CO₂ ice cleaning (ICE); 2) a combination of acetone, methanol and isopropanol (AMI) in that order, heated ultrasonically at 55 °C for 5 min each; or 3) DI water rinse designated as "None" in the flow chart below. Removal of metal ion contaminants from the KOH etch was achieved either by sequential RCA cleanings [14] – [RCA I (30% NH₄OH: 30% H₂O₂: DI H₂O – 1:1:5), followed by RCA II (conc. HCl: 30% H₂O₂: DI H₂O – 1:1:5) both at 75 °C for 10 min each] or by the Piranha (P) clean (conc. H₂SO₄: 30% H₂O₂ – 3:1) for 5 min at the intrinsic exothermic temperature of 80 °C. The experimental design is shown in Scheme 1.

The experiment largely consists of two main groups of samples, one of which received SDE and the other did not. These two sets of samples were then treated to AMI, ICE or a simple DI water rinse. Finally, each of the three sub groups was treated to two types of wet chemical treatment – RCA I & II or Piranha. The samples were then passivated by immersion in 0.01 mol/dm³ quinhydrone-methanol solution at room temperature for approximately 20 min before QSSPC lifetime measurement.

Secondly, an experimental matrix was designed towards simplifying the wafer cleaning process, and reducing the number of steps, by identifying which process steps are critical to producing high quality devices. The impacts of surface degreasing, organic removal and SDE on surface texturing were investigated. We considered four scenarios with



Scheme 1. Experimental flow chart for wafer cleaning



Scheme 2. Processing sequence for the four batches of samples used for wafer cleaning /texturing study.

no prior wafer treatments – Group 1 (AMI only), Group 2 (Piranha only), Group 3 (both AMI and Piranha, our standard process), and Group 4 (DI water). In this experiment, KOH was substituted with HNA (10% HF: conc. $HNO_3 - 1:10$) for the SDE avoiding introduction of K⁺ and eliminating the need for more complex RCA cleanings. The overall reaction of HNA with Si is given as [15]:

$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_{6(aq)} + 4NO_{(q)} + 8H_2O$$
(2)

Orientation-dependent surface texturing was achieved using a mixture of 8 ml, 25% w/w aqueous tetramethylammonium hydroxide (TMAH), 18 ml isopropanol (IPA) and 175 ml DI water, heated at 75–80 °C and accompanied with ultrasonic agitation [7]. Texturing was accomplished in two phases -20 min agitation-assisted creation of nucleation sites and another 20 min etch time without agitation, making a total of 40 min in TMAH. The samples were then rinsed in DI water with intermittent IPA spray, after which they were cleaned in piranha to completely remove TMAH residue and were dipped in 10% HF for oxide removal. The four different wafer-cleaning/texturing sequences used for this study are illustrated in Scheme 2.

Group 1: samples were treated with acetone, methanol and isopropanol (AMI) and rinsed in DI water.

Group 2: samples were treated with piranha (H₂SO₄: H₂O₂ - 3:1) and rinsed in DI water.

Group 3: samples were treated with standard solvents plus piranha (AMI + P) and rinsed in DI water (Std. process).

Group 4: samples were only rinsed in DI water.

XPS was carried out using a Thermo Scientific K-Alpha⁺ surface analysis tool and was used to characterize the wafer surface composition at three unique points – after particle/organic removal step, after HNA etch and after TMAH texture, designated as XPS-1, XPS-2 and XPS-3 respectively. The XPS tool, with known x-ray energy and work function, was used to generate a spectrum of kinetic energy and binding energy for each element on the wafer surface according to Eq. (3):

$$KE = hv - BE - \varphi_s \tag{3}$$

where $h\nu$ is the photon energy, BE is the binding energy of the atomic orbital from which the electron originates, and ϕ_s is the work function of the spectrometer. The samples were exposed to mono-energetic xrays from an aluminium anode that interacts with surface atoms, giving rise to emitted electrons that were detected and analysed. All analysis was carried out under UHV conditions with typical operational pressure of 1×10^{-9} mBar. For each XPS experiment, a qualitative survey scan is first carried out at low resolution to identify all the elements present on the wafer surface. Then, a more thorough, high-resolution, quantitative scan was done for each elemental component identified in the survey scan. Quantitative data used in this analysis was obtained from the area under each elemental peak. Scan parameters for both low and high resolution scan is shown in Table 1.

The experimental data was then fitted with a model using CASA XPS software package [16] after loading the appropriate relative sensitivity factor (RSF) from an element library containing RSFs for different XPS transitions [17]. The detection limit of our XPS is 0.1 at%, therefore any chemical residue less than 0.1 at%, which is less than a monolayer, will not be detected [18]. Atomic percent by XPS was determined by using the ratio of total area of that element to the area of all elements weighted by sensitivity factor using Eq. (4):

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