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Novel non-metallic non-acidic approach to generate sub-wavelength surface structures for inline-diffused multicrystalline silicon wafer solar cells

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ABSTRACT

One of the main restrictions on further enhancement of the multicrystalline silicon (multi-Si) wafer solar cell efficiency is the high reflectance loss from the front surface. Double-texturing, including a micro-texturing by conventional isotropic acidic-texturing followed by nano-texturing using sub-wavelength structures (SWS), provides a possibility to remove this limitation. However, presently available double-texturing processes involve multiple and high-cost nano-texturing process steps and thus have not become industrially viable. This study presents an improved double-texturing process and reports its successful implementation using low-cost inline-diffusion and non-acidic 'SERIS etch' etch-back technology. The process is based on reactive ion etching (RIE) as a metal-free nano-texturing step, along with the conventional acidic iso-texturing process. The process is optimised based on effective minority carrier lifetime and weighted average reflectance (WAR) measurements, on 156 × 156 mm^2, industrial-grade, p-type multi-Si wafers. This optimised double-textured SWS surface has a WAR of 3.2% after silicon nitride deposition, which is significantly lower than that of conventional acidic iso-textured wafers (WAR of 6–7%). However, this optimised surface maintains the same values of the effective minority carrier lifetime as for the reference conventional acidic-textured multi-Si wafers. The optimised nano-texturing recipe is also successfully applied to alkaline-textured monocrystalline silicon wafers.

1. Introduction

The worldwide photovoltaic (PV) production is presently dominated by multicrystalline silicon (multi-Si) wafer solar cells and its demand is increasing each year [1]. However, industrial multi-Si solar cells have lower efficiencies than monocrystalline silicon (mono-Si) solar cells. One of the major contributors to this lower efficiency is the lack of a viable, high-performance multi-Si texturing process, comparable to the standard alkaline pyramidal texturing [2,3] used on its mono-Si counterparts. Lower performance front surface texturing is associated with higher reflection losses from the solar cell surface, resulting in a loss in short-circuit current density (J_{sc}). For <1 0 0> oriented mono-Si wafers, anisotropic texturing in an alkaline/alcohol wet chemical solution generates random pyramid structures due to the preferential etching of the <1 0 0> crystal orientation over the <1 1 1> crystal orientation [3,4]. However, the random nature of crystal orientation of multi-Si wafers does not allow uniform formation of such structures. Presently, isotropic texturing in acidic wet chemical solutions is used in the PV industry for multi-Si surface texturing [5], resulting in a scalloped surface with rounded features. However, this texturing is not as effective at lowering surface reflectance as alkaline texturing on mono-Si. Generally, alkaline textured mono-Si and acidic textured multi-Si wafers have their weighted average reflectance (WAR) in the range of 2–3% and 6–7% in air, respectively [3,5], after deposition of an anti-reflection coating (ARC) of silicon nitride (SiN$_x$). Here, WAR is weighted using the Air Mass 1.5 Global (AM1.5G) solar spectrum over the 300–1000 nm wavelength range.

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As a “dry” (i.e. no wet chemistry) alternative for the isotropic multi-Si texturing process, reactive ion etching (RIE) has received increasing attention in recent years [6–11] to further reduce reflection losses from multi-Si wafer solar cells. Its main benefits are very low reflectance losses, the possibility of single-side texturing, reduced material loss, and reduction of chemical waste [6–11]. However, challenges associated with increased surface recombination (due to increased surface area) and relatively high equipment costs have been a barrier for the implementation of RIE texturing in most commercial solar cell production lines [9–11]. Moreover, during RIE texturing, nano-spikes are formed on the Si-surface, which typically requires an additional pre-diffusion acidic or alkaline process to eliminate the detrimental effect of the nano-spikes on the solar cell electrical parameters [7,8,12]. This process is referred to as damage removal etching (DRE).

Another alternate low reflecting Si surface is generated by a new type of textured surface, known specifically as sub-wavelength structure (SWS) [13–19]. This structure involves textured surfaces with features smaller than the wavelength of light of interest, which acts as surface-relief grating [13]. It behaves as an anti-reflecting surface which can suppress the Fresnel reflection substantially over a wide spectral bandwidth and a large field of view (i.e. a wide range of incident angles) [13–15]. Given these advantages, the SWS have been applied to light emitting diodes [16], lasers [17], optical elements [18] and transparent glasses [19]. Due to its wide-angle and wide-band anti-reflecting properties, researchers have investigated its possible use for PV applications [20–23]. Several techniques, such as laser-interference lithography, nanoimprinting [20], and metal-assisted etching [23–26] have been applied to fabricate SWS structures on the front surface of Si solar cells.

Recently, a combination of micro-texturing (acidic or alkaline) and nano-texturing processes, referred to as ‘double-texturing’ in the following text, has gained significant interest among researchers [26–29] due to its potential to further decrease the emitter surface reflectance. Xiu et al. [26] deposited a thin discontinuous layer of gold (Au) nanoparticles by electron-beam evaporation onto micro-textured (alkaline textured) mono-Si wafers. The nanostructures, formed after Au etching, yielded WAR values in air of 3.8%. Chang et al. [27] deposited indium-tin-oxide nano-whiskers by electron-beam evaporation on tube-diffused alkaline textured c-Si wafers after ARC SiN_x deposition and reported an increase of J_{sc} due to the increase in the cell’s long-wavelength spectral response. Toor et al. [28] applied a wet chemical deposition of Au and used metal etching to form nanostructures on pyramidal mono-Si wafer surfaces to improve the blue response of the solar cell, while Dimitrov et al. [29] generated nanotextures on pyramidally textured mono-Si wafers using electroless deposition of silver (Ag) nanoparticles followed by Ag etching.

Despite the low reflectance achieved by the double-texture methods reviewed above, they all have the drawback of requiring deposition of costly, sacrificial metals and subsequent wet chemical metal etching processes. The use of metals presents the potential for undesirable metallic contamination of the wafer surface before the subsequent high-temperature diffusion, thereby requiring an additional pre-diffusion surface cleaning process. These features ultimately combine to reduce the industrial applicability of metal based double-texturing. Of importance to the context of the present paper, these processes have only been applied on mono-Si wafers.

In the present paper we report a novel, metal-free and non-acidic double-texturing approach and apply it to inline-diffused 156 mm square multi-Si and 156 mm pseudo-square mono-Si p-type wafers. The micro-texturing is performed by a standard acidic solution for multi-Si [5] or alkaline solution for mono-Si [3], while the nano-texturing is accomplished by RIE without requiring any pre-diffusion DRE step. The proposed process successfully incorporates three novel concepts. Firstly, no pre-diffusion DRE is applied to the RIE nano-textured surface; secondly, low-cost inline diffusion is applied to the final RIE -textured Si surface; thirdly, a single-step non-acidic emitter etch-back process, the ‘SERIS etch’, is applied to perform simultaneous post-diffusion DRE. Following this method, the final ‘double-textured’ emitter surface is obtained. Using scanning electron microscopy (SEM), a detailed surface morphology study is carried out on wafers textured using a range of RIE texturing conditions. The double-textured surface is further optimised via an effective minority carrier lifetime study on symmetric samples. They were prepared using an inline-diffused emitter, DRE/etch-back [30] and a densified dielectric surface passivation stack on both sides of the wafers. The optimised double-textured multi-Si wafers yield a WAR value of 3.2% (after diffusion and SiN_x ARC deposition) and show a decreased surface reflectance both in the short and long wavelength range of the useable solar spectrum.

2. Experimental details

2.1. Optimisation of the double-textured inline-diffused emitters

2.1.1. Formation of micro-textured surface

For the industrial-grade multi-Si wafers (156 mm square, boron doped, p-type, 1.1–1.2 Ω cm resistivity, ~160–180 μm thick), a standard wet-chemical acidic-texturing (i.e., micro-texturing) step was performed in an industrial inline wet chemical process tool (RENA, InPilot). The process consisted of three major steps. Firstly, isotropic texturing was carried out with a mixture of hydrofluoric acid (HF), nitric acid (HNO_3) and de-ionised (DI) water at a temperature of 7–8 °C. Secondly, the parasitic porous silicon produced during iso-texturing was removed using 5% potassium hydroxide (KOH) solution at a temperature of 20 °C. Finally, the wafers were cleaned in a hydrochloric (HCl)-HF solution to remove any metal contamination left by the KOH solution. The wafers were then rinsed with DI water and dried.

For mono-Si wafers (156 mm pseudo-square, Cz, boron doped, p-type, <1 0 0> orientation, ~1 Ω cm resistivity, ~170 – 190 μm thick), the micro-texturing (i.e., alkaline-texturing) process started with saw damage etching in sodium hypochlorite (NaOCl)-KOH solution [31], followed by texturing in an alcoholic alkaline solution at 80 °C [3] to generate a random and laterally uniform pyramidal texture. After texturing, all wafers were neutralised in 1:1 HCl and DI water solution at 60 °C for 10 min, followed by a dip in dilute 5% HF solution, DI rinsing and drying.

2.1.2. Formation of nano-textured surface

The nano-texturing for both types of wafers was performed by RIE in a MPS 2200 Mini-Plasma system (JLS Designs). The process was optimised by varying the plasma power, chamber pressure, the ratio between the sulphur hexafluoride (SF_6) and oxygen (O_2) process gases, and the Si etching time. The chamber size allowed processing of four wafers simultaneously in each run.

2.1.3. Fabrication of lifetime samples for process optimisation

In order to investigate the impact of the texturing on the effective lifetime, symmetrical lifetime test structures were fabricated. As a reference group, micro-textured (acidic-textured) multi-Si wafers were processed together with the double-textured samples. An industrial inline diffusion furnace (Despatch, DCF-3615) was used with a phosphoric acid (H_3PO_4) dopant source. After an atmospheric plasma pre-treatment step at the entry to the doper (to form a hydrophilic Si surface), a spray-on H_3PO_4: ethyl alcohol dopant source was applied uniformly to both sides of the wafer at a rate of 30 cm^3/minute (min). The diffusion was performed at a belt speed of 390 mm/min using a peak diffusion temperature of