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TMAH-textured, a-Si/c-Si, heterojunction solar cells with 10% reflectance

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ABSTRACT

Single-polished c-Si (1 0 0) wafers were textured in aqueous solutions with varying concentrations of tetra-methyl ammonium hydroxide (TMAH). The resulting surface reflectance and morphology were examined as a function of etching time and temperature, TMAH concentration, and addition of isopropyl alcohol to the solution.

The lowest reflectance, 9.8% at a 600-nm wavelength with 0.3% scattering over a 4″ wafer surface, was obtained after 40 min of etching in a 2% TMAH solution at 80 °C under 700 rpm magnetic stirring. Upon adding isopropyl alcohol to the solution, the resulting pyramids were round-edged, and 12% sample reflectance was obtained.

The results are interpreted in terms of micro-masking formation and temperature-dependent crystallographic selectivity.

The compatibility of the treatment with photovoltaic applications was evaluated by studying the performance of heterojunction solar cells, which are particularly sensitive to surface quality. A degradation of the open circuit voltage was observed in devices fabricated on surfaces featuring crooked pyramid sides. Optimised process conditions led to smooth pyramid sides and no degradation of the open circuit voltage, which indicates no sign of increased surface recombination-centre concentration. The reduced reflectance resulted in a 16% increase of the short circuit current of the solar cell device.

1. Introduction

In monocrystalline silicon (c-Si) solar cells, geometrical light trapping, which is needed to reduce the reflectance losses and increase the photogenerated current, is currently achieved by wet-etching of (1 0 0)-oriented Si wafers in alkaline solutions based on potassium hydroxide (KOH) and isopropyl alcohol (IPA). Such random texturing obtained by chemical etching is photolithography-free, feasible for industrial production as it allows for simultaneous texturing of several wafers, and yields reflectivity values as low as 13% in the visible wavelengths [1]. This procedure suffers from K contamination of the silicon surface, which is detrimental to the carrier lifetime in microelectronic devices. For this reason, c-Si texturing using solutions based on sodium hydroxide (NaOH) and tetra-methyl ammonium hydroxide (TMAH) have recently attracted some interest [2–4]. TMAH is widely used in Si micro-machining when anisotropic etching is required. Indeed, Papet et al. [3] found that the oxide charge in SiO_2 grown on Si surfaces textured by TMAH is one order of magnitude lower than on KOH-textured Si. Some experiments on heterojunction (HJ) solar cells fabricated on c-Si textured in TMAH [4] and NaOH+IPA-based solutions [2] have been performed.

Nevertheless, a suitable process involving TMAH has not yet been established for photovoltaics. To our knowledge, 13% is the lowest hemispherical reflectance reported after TMAH texturing [3,4] with residual issues concerning reproducibility, homogeneity, and multi-wafer processing.

The electronic properties of the textured Si surface are particularly important in the case of HJ solar cells, in which an amorphous silicon (a-Si) emitter is deposited on top of the wafer surface. This implies that the p/n junction interface is no longer at a certain depth inside the wafer but rather is located right at the c-Si surface [5], thus highlighting the importance of developing a K-free chemical texturing process prior to emitter deposition.

Another issue to be considered when texturing is applied to solar cell devices is surface morphology. Because it is not a critical issue for the fabrication of conventional, diffused-junction solar cells, the study of the effect of different etching parameters of chemical texturing has up to now been limited to the optical properties. However, in the case of HJ solar cells, because of an emitter thickness of the order of 10 nm, i.e., much thinner than in

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standard diffused-junction devices, surface morphology represents one of the major concerns. In fact, it has been observed that microscopic surface features might give rise to non-uniformity in the deposited layers or local epitaxy at the bottom of the pyramidal valleys that can act as shunt paths, leading to high leakage current and to the degradation of the cell open-circuit voltage (V_{oc}) and fill factor (FF) [6]. This observation confirms what has been previously reported in HJ solar cells on polished (1 0 0) c-Si [7,8]. In that case, defective epitaxy on p-type a-Si/intrinsic epitaxial Si/n-type c-Si was shown to increase the interface recombination, which severely affected the V_{oc} of the HJ devices.

For this reason, in order to correlate texturing conditions with surface morphology and device performance, we report the characteristics of HJ devices fabricated on different TMAH-textured c-Si substrates.

In the past, much effort has been dedicated to anisotropic etching characterisation and modelling. According to Refs. [9,10] pyramid formation on (1 0 0) oriented surfaces is believed to be a consequence of a sort of micro-masking effect attributed to metal impurities, hydrogen bubbles, Si or SiO_2 precipitates, and reaction products, combined with favourable conditions of relative stability of the edges, high stability of the facets and high reactivity of the bottom floor surface. At high concentrations of the etching compound, the relative stability of the different sites of the pyramids is changed, and pyramid formation is inhibited. Micro-masking is referred to as the joint effect of insoluble compounds or stable agents, which prevent silicon surface etching on the atomic scale.

However, the experimental conditions normally employed [11,12] are generally not suitable for anti-reflective purposes, because in microelectronics the formation of pyramids, often referred to as hillocks, should be avoided. For this reason, in this paper, pyramid evolution as a function of TMAH dilution in water, etching temperature and time, and addition of IPA to the solution was studied with the aim of minimising the surface reflectance and creating a surface morphology suitable for HJ solar cell fabrication.

The process parameters were correlated with spectral hemispherical reflectance. The surface morphology was studied by means of Scanning Electron Microscopy (SEM). A correlation between surface morphology and solar cell performance was obtained by measuring the current–voltage (*I*–*V*) characteristics under AM1.5 G illumination of HJ solar cells fabricated on a set of textured surfaces. Results obtained for polished substrates are reported for comparison.

2. Experimental

Single-polished c-Si (1 0 0) wafers of (360 ± 20) μm thick, n-type, were textured in a solution of 25% commercial TMAH and high purity (18 MΩ) deionised (DI) water, with the addition of electronic grade IPA in some cases. The native oxide was removed in $HF:H_2O$ 0.5% for 5 min before etching. Experiments were carried out in a 1 l capped Teflon vessel to limit evaporation. The set-up allows simultaneous etching of three 4″ wafers in a vertical position. Temperature and agitation control was attained by inserting the vessel in a heater provided with a mantle and magnetic stirring. All processes were carried out under 700 rpm magnetic stirring. In the following, the name of the etching solution represents its TMAH concentration: solutions containing 2%, 5%, and 10% TMAH in water are labelled solution "2%", "5%", and "10%", respectively. The parameters under investigation include: etch temperature between 70 and 90 °C, etch duration ranging from 1 to 40 min and IPA concentration in the solution (0%, 2%, 4% and 6%).

The surface hemispherical reflectance after etching was measured using an Avantes fibre optics spectrophotometer equipped with an integrating sphere capable of collecting high-angle reflectance up to 74°. Measurements were carried out on several positions on the wafer surface, both on the front and on the back side, in order to evaluate the uniformity. However, all data reported in the following refer to the front side. The surface morphology was analysed by a Zeiss Gemini 1530 Scanning Electron Microscope.

Table 1
PECVD deposition conditions used in HJ solar cells fabrication: plasma frequency and power density, substrate temperature, gas pressure, gas flow rates.

Layer	*ν* (MHz)	*P* (mW/cm^2)	*T* (°C)	*p* (hPa)	SiH_4 (sccm)	B_2H_6[a] (sccm)	PH_3[b] (sccm)	H_2 (sccm)
p a-Si:H	13.56	28	120	0.95	2.5	8	–	13.5
n^+ μc-Si	13.56	111	170	1	2	–	2	100

[a] 0.5% diluted in H_2.
[b] 2% diluted in SiH_4.

The geometrical light scattering of textured surfaces was studied using a HeNe laser (radiation wavelength 632.8 nm). The angle of incidence was varied by mounting the samples on a rocking stage. The reflected-diffused light was projected on a hemispherical translucent screen with a slot aperture for the laser beam covering the samples.

HJ solar cells on polished and textured substrates were fabricated by plasma enhanced chemical vapour deposition (PECVD) on CZ Si, n-type, 1 Ω cm. The native oxide was etched in 0.5% diluted HF before the introduction in the PECVD vacuum system. Separate chambers were used for the deposition of n-type and p-type layers. The deposition conditions, which are the same for both polished and textured surfaces, are reported in Table 1. Solar cells $(1 \times 1)\,cm^2$ in size were fabricated using the Ag/ITO/p a-Si:H/n c-Si/n^+ μc-Si/Al structure. The Ag front grid and the Al back contact were deposited by vacuum evaporation. The ITO film was deposited by RF (13.56 MHz) magnetron sputtering at 0.5 W/cm^2 power density in a 0.021 mbar, ultra-pure argon atmosphere at 250 °C. To compensate for the lower sputtering deposition rate on sloping surfaces, the duration of the ITO deposition on the textured substrates was 1.4 times longer than on the polished samples. Reflectance measurements confirmed that with the longer deposition time, the layer thickness was the same as on the polished samples. The cells were then annealed for 1 h at 250 °C in air.

I–*V* measurements were performed at room temperature using a solar simulator equipped with an Oriel Instruments, model 6271 1000-W Xenon lamp providing AM1.5G, 1000 W/m^2 irradiation. The intensity of the incident light was monitored using a monocrystalline silicon solar reference cell calibrated by VLSI Standards Inc., with a quartz window and a thermocouple temperature sensor. The device edges were masked to shadow the regions not included in the active area. A four-contact configuration was used to separate the current and voltage probes.

3. Results

3.1. Optimisation of TMAH etching process

The TMAH etching process has been optimised by evaluating the hemispherical reflectance at a wavelength of 600 nm (*R*). Fig. 1 reports *R* as a function of the etching time at 80 °C and "2%" TMAH concentration. A small, but non-zero, local decrease of *R* can be observed even after 1 min of etching, indicating that pyramid formation occurs as soon as the etching starts. *R* decreases rapidly between 1 and 15 min of etching, and then it stabilises around 10%.