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Surface characterisation of wafers for silicon-heterojunction solar cells

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Abstract

Silicon-heterojunction cells represent a fast-growing, very promising field in photovoltaics. The key issues from the scientific and technological point of view are directly related to the quality of the junction interface (i.e., to that of the wafer surface just before thin-film deposition). The chemical purity of this surface and its dependence on HF chemical etching have been studied by XPS. Possible surface damage has been checked by SEM. Polished, rough and textured wafers have been tested. Textured samples have impurities derived from the previous pyramid-etching process. A brief (2 min) dipping in very diluted (only 1%) HF is enough to remove the 5-nm native-oxide layer. More aggressive treatments only increase surface reactivity. No surface damage is appreciated in the SEM images, not even in those of the samples etched with the highest concentrations and/or for the longest times.

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Keyword: Surfaces and interfaces

1. Introduction

Silicon-heterojunction solar cells have been gaining interest and market share in the last years. In a very short time, this technology has been able to reach 21% lab-scale efficiency [1] and 6% of the whole world photovoltaic production [2] by combining the good properties of crystalline or multicrystalline silicon with the advantages of thin-film silicon technology.

In contrast to the conventional cells based on thermal diffusion, silicon-heterojunction cells are basically surface- (or interface-) dominated. Junctions are not formed by doping part of a solid, but growing a thin film to a surface. This makes surface properties absolutely critical for the proper performance of the resulting device. The key role of surface treatments previous to thin-film deposition is widely reported in literature [3,4]. Studies show that making a good silicon-heterojunction cell from a textured wafer is much more difficult than preparing it from a polished one. Finding the reasons for this difference and understanding the influence of the chemical composition and microstructure of the silicon surface on cell properties is the aim of the research described in the present paper.

The work has been focused on three kinds of $\langle 100 \rangle$ p-type monocrystalline-silicon wafers, respectively, float-zone polished, Czochralski rough (not polished, not textured), and Czochralski textured. Only one type of treatment has been covered: HF at different times, applied for different concentrations. Chemical composition has been analysed by AR-XPS (angle resolved X-ray photoelectron spectroscopy) measurements and possible microstructural changes have been monitored by SEM (scanning electron microscopy).

2. Experimental procedures

Substrates have been cleaned in acetone for 2 min, cleaned again in ethanol in an ultrasonic bath for 8 min, rinsed in 18.2-MΩ cm de-ionised water (DIW) and dried with nitrogen.

The native oxide on the surfaces has then been removed with a HF:DIW bath (diluted hydrogen fluoride in 18.2-MΩ cm-resistivity DIW) at ambient temperature. Different treatment times (from 0 to 15 min) have been tested for 1%

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HF, and different HF concentrations (from 0 to 40%) have been assessed for a fix 2-min immersion time.

XPS measurements have been used to analyse the influence of the HF wet treatment on the surface chemical composition for each type of substrate. In order to avoid the regrowth of the native oxide layer, the samples have been immediately analysed after the HF treatment. Substrates have been excited with a Mg Kα X-ray source ($h\nu = 1253.6$ eV) operated at 300 W input (12 kV and 25 mA). Pass energy was 89.5 eV for general spectra (0–1100 eV) and 44.75 eV for high-resolution ones. Surface analyses have been carried out at 10^{-9} Torr base pressure and 1 mm^2 spot size by using the angle-resolved XPS technique at 20, 45 and 70°. Such a non-destructive method is based on the fact the photoelectron flux angles closer to the direction perpendicular to the surface has higher contributions from the deeper layers. In this way, information about surface and subsurface composition of the samples can be obtained. Nevertheless, since all the trends in the evolution of the XPS spectra have been found to be insensitive to the incidence angle, only 20°-incidence data are reported. The composition underneath is studied with fix-angle XPS (45°) on the samples subject to 3 kV Ar^+ sputtering at 10^{-7} Torr. Sputtering rates were estimated to be 60 Å/min from a Ta_2O_5/Ta sample of known thickness. Atomic concentration has been determined by evaluating the corresponding peak area weighted by element sensitivity factors. In order to take into account the charging effects on the measured binding energies, all the spectra have been referred to the C 1s line (binding energy 285.0 eV).

The morphological properties of textured and rough substrates have been analysed by SEM. The surfaces of the samples for imaging applications must be electrically conductive and unpolished.

3. Results and discussion

3.1. Impurities

The chemical composition of the crystalline-silicon surface has a critical influence on the density of interface defects and therefore on device performance. AR-XPS has therefore been used to analyse the atomic composition of the surface before and after HF treatment for each of the three kinds of wafers under study. Before HF etching treatment the results at 20° incidence angle (see Table 1) show that some chemical elements, such as Ca and Al are present on the surface of textured samples whereas absent from those of polished or rough wafers. These elements do not disappear with the subsequent HF etching. The difference between the surface composition of the three wafers studied is attributed to the chemical-etching treatments used in the texturing process and may partly account for the difficulties encountered in making good silicon-heterojunction cells from textured wafers. Additionally, fluorine appears on the surface of both textured and rough untreated wafers. The reason for this is very probably the cleaning treatment applied to wafers just after their slicing from the ingot, which includes the immersion in HF in an ultrasonic bath. The fluorine concentration does not only remain, but even increases with the HF concentration and etching times (see Fig. 1). This result suggests the convenience to apply the lowest HF concentrations and etching times possible, being compatible with the removal of the native oxide.

Table 1
Atomic concentrations on the surfaces before HF treatment analysed by 20°-AR-XPS

Elements	% Atomic concentration		
	Textured	Rough	Polished
Si 2p	36.5	46.0	37.4
C 1s	11.1	26.0	25.9
0 1s	49.6	27.4	36.8
F 1s	0.5	0.6	–
Ca 2p	0.8	–	–
Al 2p	1.6	–	–

3.2. Native oxide

In all cases the native oxide disappears with a brief dipping in 1% HF for 2 min at ambient temperature. The average thickness has been estimated by XPS depth profiles by taking into account the point at which the ratio of oxygen

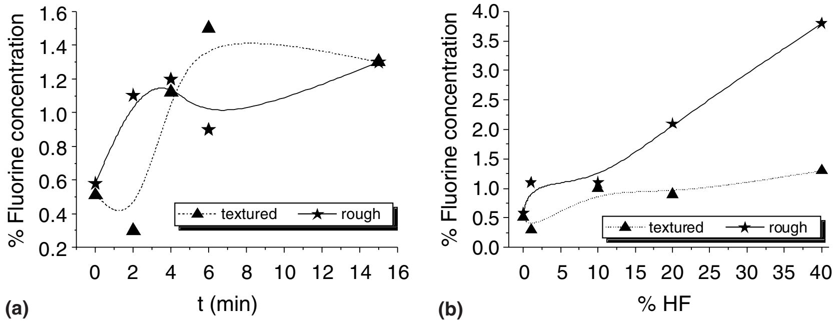

Fig. 1. Fluorine concentration on the wafer surface after etching with HF diluted in DIW: (a) as a function of etching time for 1% HF and (b) as a function of HF concentration for 2 min etching time.

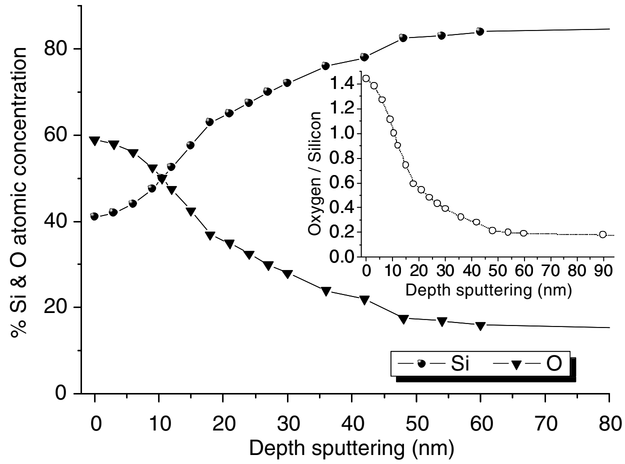

Fig. 2. Depth profile at 45° incidence angle for a textured wafer. Si and O normalized to 100%.

and silicon concentration is lower than one. The estimated thickness of the SiO_2 layer before etching is 5 nm in polished and rough wafers, whereas this thickness goes up to 15 nm in textured samples (see Fig. 2). This result is, however, affected by limitations in the determination of thicknesses by this method in non-flat surfaces. This inaccuracy may be attributed to shadowing and re-deposition effects [5] that can be partly eluded by using sputtering with two ion guns [6]. This is illustrated in the inset of Fig. 2, which shows a long tail, attributed to oxide areas in positions shaded with respect to the primary ion beam.

The effect of the chemical etching with HF is summarised in Fig. 3. In all substrates, increasing either concentration or etching time, causes a reduction of the oxygen concentration associated with the disappearance of the native-oxide layer. Concurrently, a rise of the carbon concentration on the surface is detected. This effect, more appreciable in polished wafers, is ascribed to an enhancement of the chemical reactivity of the crystalline-silicon surface. Applying the criterion of the highest silicon concentration on the surfaces, the best treatments (those yielding the most efficient native-oxide removal) found for each substrate are:

- 1% HF:DIW for 4 min or 10–20% HF:DIW for 2 min in textured samples.
- 1–20% HF:DIW for 2 min in rough samples.
- 1% HF:DIW for 2 min in polished samples.

The use of higher concentrations or etching times not only does not lead to a more efficient cleaning of the surface, but furthermore enhances its reactivity.

3.3. Surface damage

SEM analyses were performed on textured and rough samples (Fig. 4). The images show no changes in surface

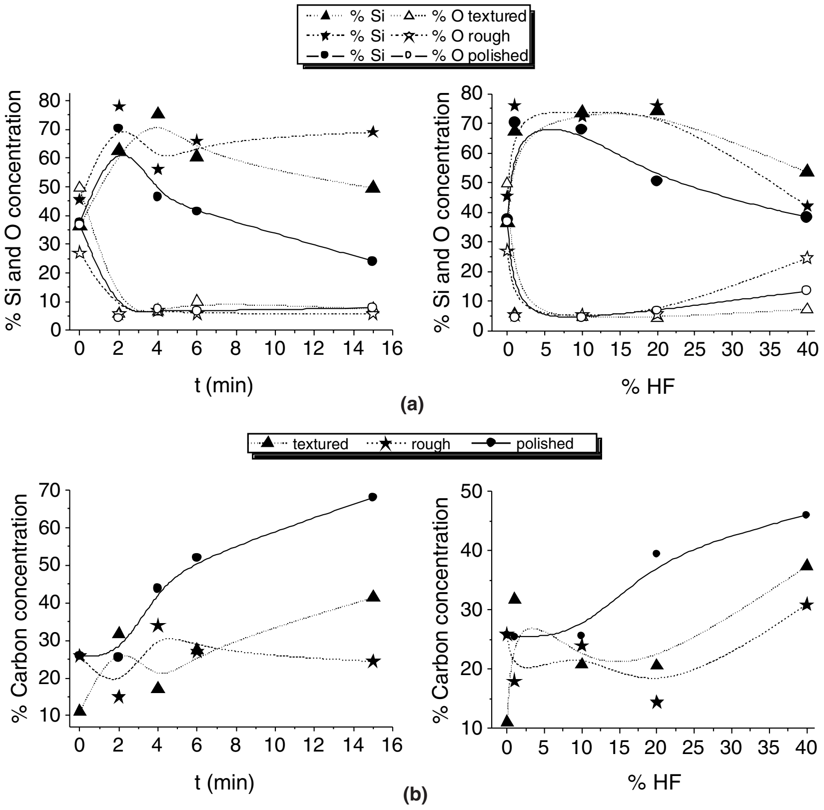

Fig. 3. C, Si and O concentration deduced from XPS at 20° incidence angle after etching with HF diluted in DIW: (a) as a function of etching time for 1% HF and (b) as a function of HF concentration after 2 min etching time.

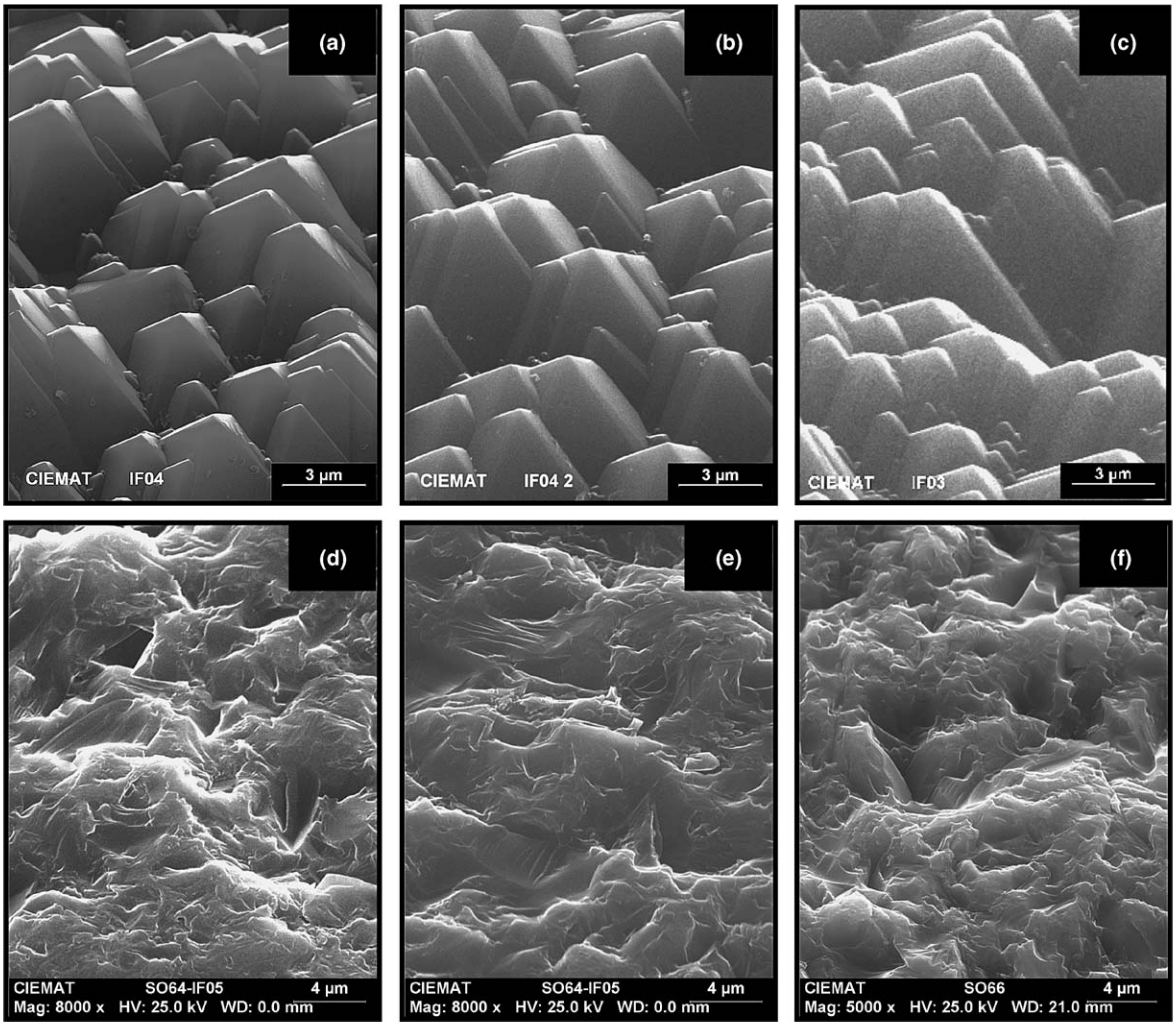

Fig. 4. SEM images at 30° incidence angle (a), (b) and (c) are textured silicon surfaces and (d), (e) and (f) are rough silicon surfaces. (a) and (d) before HF treatment, (b) and (e) after 40% HF for 2 min, (c) and (f) after 1% HF for 15 h. In textured samples, the sides of the pyramids are intersecting (1, 1, 1) planes within the crystal structure of the silicon.

morphology associated with HF etching within the concentration and etching-time ranges studied. This is in contrast to what is reported in the literature for dry etching with $CF_4 + O_2$ plasmas [7,8].

4. Conclusions

The chemical purity of wafer surface just before deposition is a critical factor affecting dramatically the performance of silicon-heterojunction cells. The surfaces of three different types of wafers have been analysed and compared, and the effect of hydrofluoric-acid etching on them has been studied. Untreated textured wafers show surface impurities (Ca, Al) probably incorporated during the texture-etching process. This may help explain the greater difficulty in making silicon-heterojunction cells from textured wafers with respect to non-textured ones. The native-oxide layer thickness has been estimated to be about 5 nm by XPS depth profiles. HF (1%) in de-ionised water for 2 min is enough to remove it. Higher concentrations or etching times should not be used in order to avoid an enhanced surface reactivity evidenced by the incorporation of carbon. No surface damage has been appreciated by SEM on any of the samples of this study, in spite of the wide range of concentration and etching time covered. This suggests that HF chemical etching is probably less critical than plasma dry etching.

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