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Direct imaging of dopant distributions across the Si-metallization interfaces in solar cells: Correlative nano-analytics by electron microscopy and NanoSIMS

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ABSTRACT

The overall efficiencies of screen printed monocrystalline Si solar cells are limited by electrical losses across the Si-metallization interface. The process of metallization affects the emitter and space charge region of the solar cell, particularly with respect to the dopant distributions. Until now, direct imaging of dopant distributions across the interface has not been reported mainly because the concentrations of dopants are far below the detection limit of conventional analytical tools. In the present study, we harness the high-resolution (100 nm) high-sensitivity chemical imaging with Nano Secondary Ion Mass Spectrometry (NanoSIMS) and correlate with microstructural and electrical properties to elucidate the factors limiting the overall cell efficiencies. We analysed two sets of p-type solar cells fabricated from identical starting materials, the only difference being the firing temperature. It was found that the overall efficiency of cells fired at 900 °C was ~17% while the efficiency of cells fired at 960 °C was only 13.6%.

In phosphorus (P) ion maps, the P emitter structure was found to be well-preserved by NanoSIMS in cells fired at 900 °C, it was completely disintegrated in the overfired cells and thereby increasing the contact resistance. The passivation layer (SiN_X) was found to be disintegrated in the overfired cell and furthermore, below the metallization, a diffusion cloud was observed wherein boron (B) rich domains extend over several µm. In the overfired cell the disintegration of the SiN_X layer identified in the SEM correlated with the disintegrated emitter structure (P) analysed by NanoSIMS. This implies that the disintegration of the passivation layer leads to a diffusion of the dopants resulting in the loss of overall cell efficiency. Thus, our new comprehensive approach provides unprecedented insights into the factors limiting the overall efficiencies in solar cells.

1. Introduction

Secondary Ion Mass Spectrometry (SIMS) depth profiling has played an essential role for semiconducting devices particularly for Si solar cells technology [1], and thin film solar cells (e.g., CIGS thin film solar cells) [2–4]. New instrumentation lead to NanoSIMS, i.e. SIMS with a high lateral resolution and high sensitivity [5,6]. This new possibilities due to instrumentation yielded significant results for contamination of metals and their structural properties. The minimum beam diameter limited by ion optics is 50 nm [5,6]. NanoSIMS has been applied to analyse grain boundaries and interfaces in metals. Grain boundary segregation is a well-known effect and dramatically influences the structural properties of metals. Sulphur contamination in Ni was studied in detail and the sensitivity of NanoSIMS was estimated as 0.004 monolayers [7]. NanoSIMS was also applied to study Al alloyed with Si containing small fractions of Si. Precipitation phenomena were observed for such systems yielding particle sizes of less than 1 µm and contamination detected by NanoSIMS on the ppm scale [8].

Among the many results obtained by NanoSIMS only few deal with semiconductor technology. Since Nano-SIMS is primarily used in technology calibration and failure analysis which represents confidential information, only few published papers exist. Static random-access memory (SRAM) devices based on complementary metal-oxide-semiconductor (CMOS) technology were analysed for failure analysis purposes and structures grown in a 130 nm technology could be resolved by NanoSIMS. B, As and P doped active areas on the

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130 nm scale could clearly be identified. This shows the great potential of NanoSIMS for providing the local dopant concentration at the 100 nm scale [9]. It should be added that the lateral resolution and sensitivity both affect the minimum detection limit and that resolution and minimum detectable mass fraction have to be proven experimentally for individual cases. This is one of the purposes of this paper. The relatively large dopant concentrations in emitters of Si solar cells make NanoSIMS ideal for studying the dopant distribution in such devices.

In the past 30 years, considerable efforts have been made to improve the contact formation process of silver (Ag) thick film front side metallization in monocrystalline silicon (Si) solar cells with P doped emitters. The contact formation is mainly realized by screen printing technology, due to its simplicity, cost effectiveness and high throughput. Details of the phase forming reactions of the front side metallization by screen printing are given in Ref. [10]. Electrical losses due to front side metallization limit the efficiency of the solar cell, among which the specific contact resistance between the Si/Ag metallization interfaces is one term entering the series resistance and is sensitively dependent on the processing conditions used for the front side metallization [11].

Screen printed front side contacts show a complex Si/metallization interface. At the contact interface, Ag nanocrystals are formed at the Si surface and are covered by a glass layer containing metallic Ag colloids [12–17]. The chemical composition of the glass layer depends on the composition of the paste [15–17], and the processing parameters and might strongly affect the electrical conductivity. However, the formation of Ag nanocrystals is affected by the orientation of the Si surface and etching ability of the paste [15–17].

The influence of firing conditions on the microstructure and its effect on the contact resistance was reported in the literature [18–22], however, no systematic analysis has been carried out, particularly with respect to dopant distribution at the Si/metallization interface. Due to the high temperature firing process, atoms from the metallization are assumed to diffuse as impurities into the emitter as well as space charge region of the solar cell [23]. This in turn increases the recombination current of the emitter and space charge region of the cell, and degrades the cell efficiency.

An important factor that limits the solar cell efficiency is the electrical resistance across the Si-metallization interface. The spatial distributions of dopants across this interface play a key role in determining the overall efficiency. Until now, direct imaging of dopant (P, B) distributions across the Si-metallization interface has not been reported mainly because the concentrations of dopants are far below the detection limit of conventional analytical tools such as EDX. In the present study, we harness the high-resolution high-sensitivity chemical imaging with NanoSIMS and correlate with microstructural and electrical properties thereby giving us unprecedented insights into the factors limiting the overall cell efficiencies.

In this paper, we take a correlative approach [24], to elucidate the effects of firing conditions on the microstructure, particularly the dopant distribution across the contact interface and establish a cross-relation to the electrical measurements. For this, a combined Secondary Electron Microscopy (SEM) and Nano Secondary Ion Mass Spectrometry (NanoSIMS) study was applied to investigate the Si/Ag contact interface by mapping Si, B and P secondary ions with high lateral resolution. By this approach, we obtained unprecedented insights about the lateral distribution of the dopants both in the emitter and the space charge region and elucidated its role in determining the solar cell efficiency. With our new comprehensive analytical strategy, we uncover the underlying reasons responsible for variation in solar cell efficiencies and propose methods to optimize solar cell processing.

2. Experimental section

2.1. Solar cell processing and electrical measurements

Textured cells (#T1 and #T2) were processed on Cz grown p-type Si wafers with P doped emitters. Details of solar cell emitter and metallization processing are described in Refs. [15,25]. The metallization was realized by a screen printing technology, and front side paste (FSP1) was used to contact the P doped emitters.

Cell #T1 was processed under optimal firing condition to a set temperature of (T_{FF0}=900 °C), whereas cell #T2 was processed at a too high set temperature (overfired, T_{FF0}=960 °C), for details see Table 1. The term “optimally fired” is used with respect to the firing temperature variation for a given paste, several temperatures were applied in different batches and the cell with the best results was termed “optimally fired” in Refs. [15,16,25]. Note that the term “optimally fired” is used with respect to temperature variations for a given paste. It does not indicate an overall optimization of the metallization in terms of series, contact and parallel resistance.

The electrical properties of the large cells such as efficiencies (η), fill factor (FF), parallel (R_P) and series resistance (R_S) are listed in Table 1. These measurements were carried out by a commercial cell tester at Fraunhofer Institute for Solar Energy Systems (ISE) [15,25]. The overfired cell #T2 yielded a significantly higher series resistance (3.91 Ω cm^2) and a lower efficiency (13.6%) as compared to cell #T1. The parallel resistance of cell #T1 is low compared to cells processed with different pastes and yielding better contact performance [15,16]. The difference in parallel resistance between cell #T1 and cell #T2 is small, the difference in R_S is large.

In addition, the specific contact resistance (ρ_C) measurements were carried out by the transmission line method (TLM) on small strips (1.5×1 cm^2) at room temperature (RT). Due to overfiring cell #T2 showed a high specific contact resistance (131 mΩ cm^2), whereas cell #T1 had a small contact resistance of (21 mΩ cm^2) and higher efficiency (~17%).

2.2. Characterization techniques for small cells

The temperature dependent dark $I–V$ curves were obtained on small sized cells from 80 K to RT in an optical cryostat. From this the temperature dependent series resistance was evaluated by fitting the dark $I–V$ curve with the two diode model [11,16,26,27]. A combined SEM equipped with an Oxford Pentafet energy-dispersive X-ray detector (EDX) unit [15–17], and Nano Secondary Ion Mass Spectrometry (NanoSIMS) study was applied to investigate the Si/Ag contact interface by mapping Si, B and P secondary ions with high lateral resolution. Cells were analyzed both in plan-view and in cross-section. Details of the sample preparation are given in Refs. [15,16].

2.3. Secondary Ion Mass Spectrometry with high lateral resolution (NanoSIMS)

SIMS is particularly well-suited for the study of dopants in silicon such as B and P thanks to its possibility to detect elements in very low concentrations in depth profile mode [5]. In this study a Cameca NanoSIMS 50 equipped with a double focussing magnetic sector spectrometer was used in imaging mode [28]. The essential features of this recently available instrument are its outstanding lateral resolution together with excellent detection limits enabling the analysis of the dopants in Si. It could be shown that a lateral resolution down to 50 nm can be reached in the negative secondary ion mode under Cs$^+$ primary ion irradiation, for details see [28]. The instrument was operated with a primary Cs$^+$ source and a probe current of 1 pA with an impact ion energy of 16 keV. The secondary ion maps were acquired as 256×256 pixel images with a dwell time of 5–10 ms per pixel on fields of view of 15×15 μm^2. The instrument was tuned to resolve the mass interferences between $^{31}P^-$ and $^{30}Si^1H^-$ with a mass resolution M/ΔM above 4000 [5]. The NanoSIMS can be run at high mass resolution without significant loss of the transmission of the instrument [28]. As the coaxial optics of the NanoSIMS requires opposite polarities between the primary and secondary ions, and as a Cs$^+$ primary ion beam was used, all elements were detected as negative secondary ions. Boron was