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Factors limiting minority carrier lifetime in solar grade silicon produced by the metallurgical route

V. Osinniy [a,*], P. Bomholt [a], A. Nylandsted Larsen [a], E. Enebakk [b], A.-K. Søiland [b], R. Tronstad [b], Y. Safir [c]

[a] Department of Physics and Astronomy, Aarhus University, DK-800 Aarhus C, Denmark
[b] Elkem Solar A/S, N-4675 Kristiansand, Norway
[c] RAcell Solar A/S, DK-1820 Frederiksberg C, Denmark

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ABSTRACT

Solar grade, *p*-type multicrystalline silicon wafers with large grains from different parts of silicon ingots produced by the metallurgical route (SoG-Si) at ELKEM Solar were studied using a number of complementary methods such as microwave photoconductivity decay, deep level transient spectroscopy, transmission and scanning electron microscopy, X-ray fluorescence, and secondary ion mass spectroscopy. Wafers from the top of the ingots have uniform spatial distributions of both minority carrier lifetime (average lifetime $\tau = 3.2\ \mu s$) and concentrations of illumination-sensitive recombination centers ($N_{rc} = 3 \times 10^{10} - 2 \times 10^{11}\ cm^{-3}$) over the whole wafers. Wafers from the bottom of the ingots have regions of very low lifetimes ($\tau = 0.3\ \mu s$) and high concentrations of illumination-sensitive recombination centers ($N_{rc} = 2 \times 10^{12}\ cm^{-3}$). In the top part of the ingots the observed DLTS peaks can be attributed to copper-related extended defects, and the DLTS results from grains and grain boundaries are not significantly different. The main factors limiting the lifetime in the high lifetime regions are concluded to be illumination-sensitive recombination centers such as Fe–B pairs, B–O complexes, and Cu-related extended defects. The low lifetimes in the bottom part of the ingots are explained by a combination of several factors including high concentrations of illumination-sensitive recombination centers and of some deleterious elements (S, Na and Al), and a large amount of structural defects.

1. Introduction

Several groups have recently investigated methods for improving the electrical properties of solar grade silicon produced by the metallurgical route (SoG-Si) [1–3]. The low wafer cost and the high-volume production makes this material a very promising material for low cost solar cells. During recent years the efficiencies of solar cells fabricated from SoG-Si significantly improved and have attained values of 16–18% [4–6] approaching the highest reported efficiencies of multicrystalline Si solar cells of about 20% [7]. The SoG-Si solar cell performance is influenced by the applied processes and treatments during crystallization, wafering and cell fabrication through the type and amount of recombination centers, such as contaminations and structural defects [4]. Transition metals and their precipitates in Si are effective recombination centers as they introduce mid-gap levels in the band gap. In the case of SoG-Si the contaminations are mainly collected at the grain boundaries or intra-grain defects. From recent investigations of the influence of metal impurities on the electrical performance of grains [8–11], it is still unclear if the minority carrier lifetime is mainly limited by the total metal concentration or the chemical state and distribution of metals within the grains.

Manufacturers of SoG-Si receive raw materials from different sources and use their own, and often unique, equipments and technologies for the ingot growth. Thus, the ingots produced by different companies can differ significantly from each other by contaminants and their concentrations. Depending on the type and concentration of impurities present inside silicon wafers there are different processes which might reduce the total concentration of impurities or weaken their recombination strength. The most popular methods are gettering processes using aluminum [12,13], phosphorous [14] and SiN_x [15] as precipitation centers for contaminations. However, in order to more precisely select the gettering method it is recommended to make a quantitative and, if possible, a qualitative analysis of type and concentration of impurities present inside the as-grown silicon wafers, and to establish the nature of the most deleterious elements. In the present work we have investigated properties of as-grown multicrystalline, *p*-type silicon wafers produced by the metallurgical route by ELKEM Solar. Typical minority carrier lifetimes in as-grown ELKEM SoG-Si wafers of electrical resistivity close to 1 Ω cm vary between 3 and 20 μs and can be increased up

Abbreviations: HL area, high lifetime area; LL area, low lifetime area

* Corresponding author. Tel.: +45 8942 3730; fax: +45 8612 0740.
E-mail address: vos@phys.au.dk (V. Osinniy).

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to 30–45 μs using a phosphorous gettering process [16]. These values are comparable to those of reference multicrystalline silicon (30–70 μs) [17,18]. However, for the present investigation a special method of ingot growth was used which allows to increase artificially the concentrations of contaminations which are "standard" for ELKEM SoG-Si. Thus, the photovoltaic quality of the investigated material was purposely worsened to facilitate an assessment of the main factors which limit minority carrier lifetimes.

2. Experimental details

Multicrystalline SoG-Si, square-shaped 152×152 mm^2, thickness of about 250 μm, and resistivity of 0.5–1 Ω cm (Fig. 1), from top and bottom ends of an ingot were investigated using different methods to establish their electrical properties, and to estimate the main factors limiting, in particular, their minority carrier lifetime. Several wafers from both ends of the ingot were investigated. As the measured minority carrier lifetimes did not differ significantly in wafers from the same part of the ingot only results from two typical wafers are reported. Wafers having large grains were chosen in order to easy distinguish factors influencing the electrical properties of grain and grain boundary areas. The sizes of the selected grains varied between 3 and 9 cm^2; their crystallographic orientations were determined using X-ray diffraction. For the sequential measurements, the wafers were divided into small pieces having areas between 10 and 25 cm^2, and they were cut in such a way that every sample contained a large part of a grain and a large grain boundary area.

The minority carrier lifetime (τ) and the illumination-sensitive recombination center concentration (N_{rc}) in the SoG-Si wafers were mapped out with the microwave photoconductivity decay technique (μ-PCD) using a SEMILAB WT-2000 instrument. The penetration depth in silicon of the 904 nm laser wavelength used was about 30 μm; thus the free carriers under investigation are generated close to the surface of the sample. The surface passivation was chemically performed using an iodine/methanol solution. Before iodine passivation the sample surface was chemically polished using a CP-4 etchant ($HF:CH_3COOH:HNO_3$) for 3 min and etched in 10%-HF solution for 2 min. Subsequently, the samples were put into special plastic bags filled with the iodine/methanol solution. Air bubbles were removed from the liquid in order to provide a uniform passivation of the whole surface. In agreement with the recommendation of the instrument producer the minority carrier lifetime measurements were carried out using a bias of continuous white light of 1000 μW/cm^2. Using bias light a large number of excess carriers are continuously generated and recombine with the surface states. The surface states are thus continuously occupied, and the excess

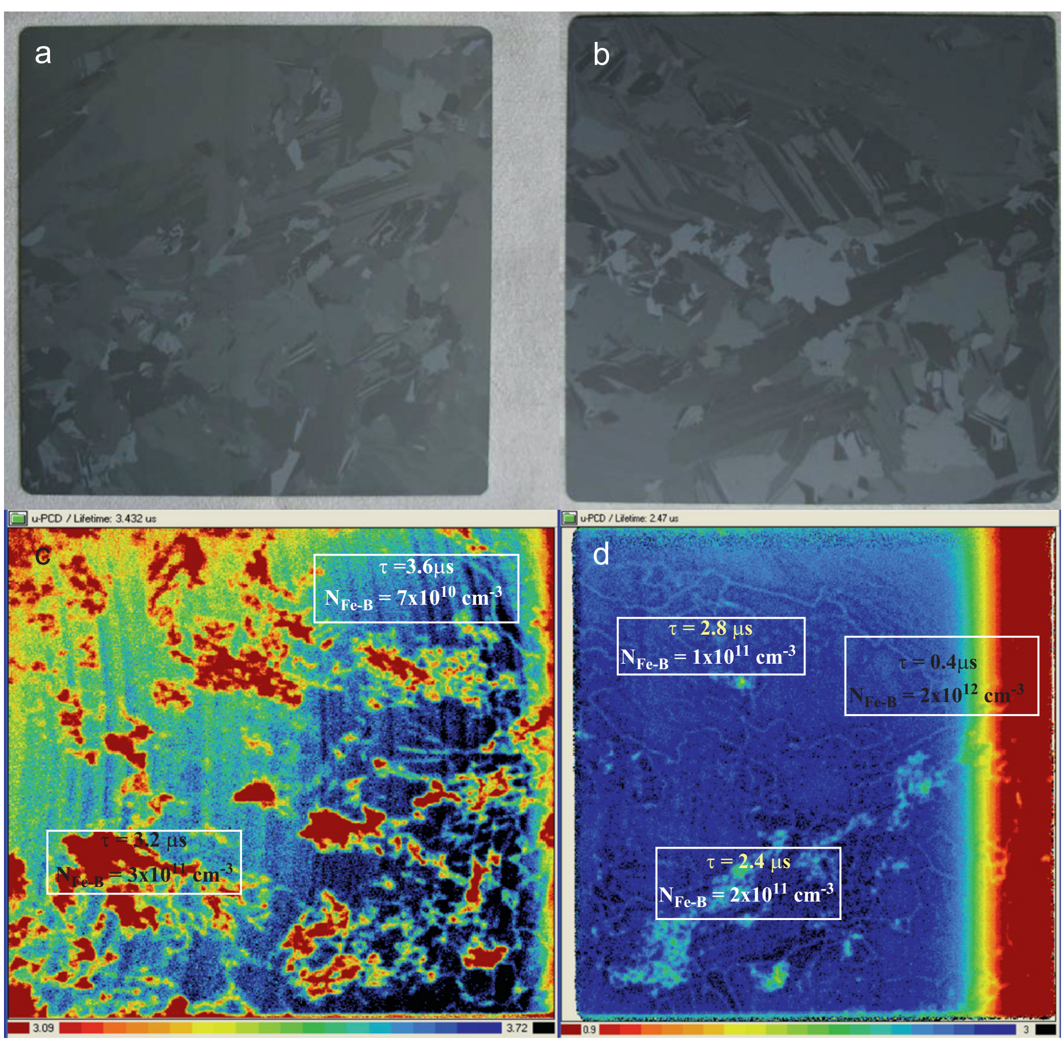

Fig. 1. Photos and minority carrier lifetime spatial distribution maps of wafers from the top (a, c) and bottom (b, d) of the SoG-Si ingot, respectively. The values of τ and N_{Fe-B} are indicated for characteristic areas.