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Microscopic origin of the aluminium assisted spiking effects in n-type silicon solar cells



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ABSTRACT

Contact formation with silver (Ag) thick film pastes on boron emitters of n-type crystalline silicon (Si) solar cells is a nontrivial technological task. Low contact resistances are up to present only achieved with the addition of aluminium (Al) to the paste. During contact formation, Al assisted spiking from the paste into the silicon emitter and bulk occurs, thus leading to a low contact resistance but also to a deterioration of other cell parameters. Both effects are coupled and can be adjusted by choosing proper Al contents of the paste and temperatures for contact formation. In this work the microscopic electric properties of single spikes are presented. These microscopic results, i.e. alterations of the local emitter doping density, the pronounced local recombination activity at the interface between spikes and Si and its influence on the charge collection efficiency, are used to explain the observed dependencies of global cell parameters on the Al content of contact pastes.

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1. Introduction

Up to now, Al is a necessity in industrial Ag thick film pastes for good contact formation on boron emitters, i.e. a low contact resistivity. The use of Al–Ag pastes for the emitter metallisation introduces a mechanism which is both, beneficial and harmful: “spiking” of an Al–Ag phase from the paste into the silicon material. Above about 660 °C, Al particles in the paste melt and the Ag matrix facilitates Al transport to the Si interface and an Al–Ag–Si contact is formed [1,2]. In contrast to the commonly used name “Al spike” for these v-shaped contacts we will use the name “Ag–Al spikes”, as the spikes consist of mainly Ag (see below). Ag–Al spikes are responsible for good contact formation. If spiking occurs through the emitter, this mechanism can lead to a Schottky-type direct contact between the metal and the silicon bulk material. The inevitable negative influence of Ag–Al spikes on global cell parameters like open circuit voltage (V_{oc}) and grid resistance has been investigated [3–5] and is confirmed within this work; the V_{oc} measured after metallisation with a standard Al containing Ag thick film paste was measured to be about 25 mV lower than the implied V_{oc} (iV_{oc}) of 660 mV measured before metallisation. Furthermore, by doubling the fraction of metallised

area, the drop in V_{oc} increased correspondingly after firing. However, the underlying local electrical properties of the spikes and their specific impact on cell performance remained unclear up to now.

To investigate the contact formation and deterioration caused by Al assisted spiking we choose a two-step approach: (1) observation of the influence of Al content in the paste on the global cell performance; (2) microscopic analyses of the local electrical properties in the vicinity of single spikes, of which the number and size scale with Al content in the paste.

2. Influence of Al content of paste

To specify the influence of the composition of the paste used for p⁺ metallisation, samples with different pastes were processed: a standard reference paste, pastes with different amounts of Al compared to the reference (without Al and with 0.5 ×, 2 ×, 4 ×, and 6 × the amount of Al compared to the standard paste), a non-contacting paste (i.e. a paste which is not fired through the passivation) and a sample without metallisation. The 6 × higher amount of Al led to a drop of cell efficiency from 18.6% to 17.2%. Both, iV_{oc} and pseudo fill factor (pFF) decrease with rising Al content of the paste (for pFF see Fig. 1, the dependence of V_{oc} is similar). In accordance to [4], a higher V_{oc} was observed using a non-contacting paste. The plot in Fig. 2 reveals a reduction of

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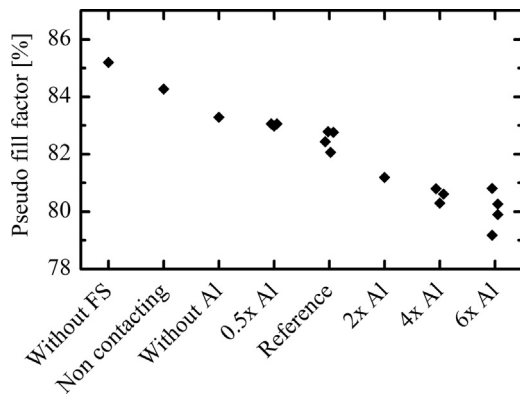


Fig. 1. Decrease of the global pseudo fill factor with increasing Al content of the Ag-Al metallisation paste.

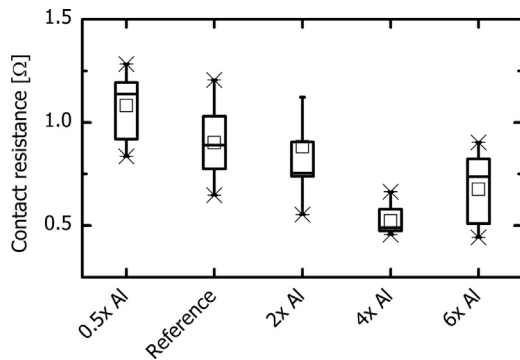


Fig. 2. Decrease of contact resistance with higher Al content in the paste.

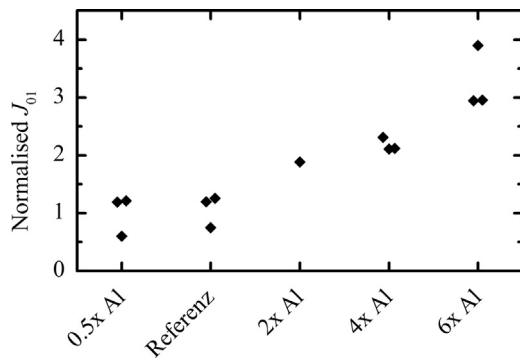


Fig. 3. Increase of J_{01} with Al content in the paste.

contact resistance with Al content in the paste. The slight increase of contact resistance with $6 \times$ higher Al content is caused by an increased line resistance, which limits the measured resistance in this case. Additionally to the decrease of pFF and V_{oc} we also observe an increase of J_{01} , which indicates a surface recombination issue in the emitter.

The observed effects can be explained postulating an Al assisted spiking mechanism [2]. The experimental microscopic proof of both the beneficial and harmful properties of Ag-Al spikes explaining the global effects is given in the following section.

3. Microscopic characterisation of Ag-Al spikes

In order to trace the observed effects of Ag-Al spikes on global parameters back to their microscopic origin, cross sections cut

from the samples are investigated in the following. The cross sections were diamond and SiC polished. The high resolution electric and spectroscopic techniques are based on a confocal microscope, which focusses a laser to a spot with diffraction limited size. Techniques with sub-micron resolution are employed by detecting:

- the scattered light: Micro-Raman Spectroscopy (μ RS) enables to map the emitter doping density at low [6] and carrier lifetime at high laser excitation [7];
- the photoluminescence (PL) of generated electron-hole pairs: from Micro-PL Spectroscopy (μ PLS) [8], the carrier lifetime can be extracted;
- the photo-generated current: Micro-Light Beam Induced Current (μ LBIC) [9].

A 355 nm laser is used in combination with a $40 \times$ lens with $NA=0.60$, PL and Raman scattered light are excited with 532 nm laser light and detected with a $50 \times$ lens with $NA=0.65$ and $100 \times$ lens with $NA=0.9$, respectively. In the case of μ PLS Auger recombination caused by the used high injection strongly reduces the diffusion length of generated carriers to below $1 \mu\text{m}$. This confinement of carriers into a small volume is enhanced by strong dilution of carriers away from the excitation spot due to their 3D diffusion and thus leads to sub-micron resolution for all methods Fig. 3.

3.1. Description of samples for microscopic investigations

A commercial Ag-Al paste is screen-printed on a random pyramid textured n-type CZ wafer with a diffused $90 \Omega/\text{sq}$ Boron emitter, $70 \Omega/\text{sq}$ Phosphorus back surface field and fired at a set peak temperature of about $905 \text{ }^\circ\text{C}$. With this temperature slightly above usual firing temperatures a further deterioration of the resulting cell is observed. In parallel, we observe an increased number and size of Ag-Al spikes on polished cross sections of these samples, presumed to be responsible for the deterioration [2]. The more pronounced influence of these enlarged spikes simplifies their microscopic characterisation.

3.2. Microscopic pre-characterisation

Fig. 4a shows a representative SE contrast image of the cross section cut of a sample. The sketch in Fig. 4c illustrates the observations: the pattern in the top part is the metallisation paste; the area in the lower part is the silicon bulk. The light band in between (dotted in grey in the sketch) is the p^+ emitter; SE contrast can be used to distinguish between areas of different types of doping [10].

Spikes are identified by their typical V shape, homogeneous filling with an Ag-Al alloy and overlap with the emitter; in the model of Al assisted spiking Si (i.e. also the emitter) is consumed during spike formation and replaced by an Ag-Al alloy. EDX confirmed the features of the Al assisted spiking mechanism (Fig. 4c): the Al content in the spikes is about 1%, which is according to [2] where Al is needed to create spikes via an Ag-Al-Si alloy phase, but where the spikes themselves consist mainly of Ag. The spikes are depicted in the sketch by the area dashed in red. Both spikes are classified as “deep”, i.e. punching through the emitter, in contrast to “shallow” spikes, which are fully located within the emitter.

3.3. Micro-spectroscopic characterisation

The doping density measured with μ RS at these spikes (Fig. 4d) supports the finding of SE contrast, that the spikes interrupt the

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