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Contact formation of front side metallization in p-type, single crystalline Si solar cells: Microstructure, temperature dependent series resistance and percolation model

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ABSTRACT

Screen printed front side contacts were investigated in single-crystalline (planar and textured) Si solar cells with n-type emitters, yielding maximum efficiencies of 18.0%. The crystallographic orientation of the Si surface and the paste strongly affect the contact formation as well as the contact resistance of the cells. For textured cells a continuous glass layer together with the formation of Ag colloids yielded a small contact resistance. Planar ⟨111⟩oriented Si yielded specifically lower contact resistance (⟨5 mΩ cm^2) as compared to planar ⟨100⟩ orientation (⟩10–40 mΩ cm^2) for different pastes. Pyramidal Ag crystals are formed only on ⟨100⟩ oriented Si, whereas lens shaped Ag crystals are grown on ⟨111⟩surfaces. From this it was concluded that the shape of the Ag nanocrystals determines the contact resistance, pyramidal Ag crystals formed on ⟨100⟩ planar surfaces yielded cells with large contact resistance and are, therefore, not considered to be necessary for a low contact resistance.

Temperature dependent series resistance measurements yielded metallic behavior for cells with the lowest contact resistance bound to a certain paste. For other pastes and processing conditions a semiconducting behavior of the series resistance was found. However, cells with significant density of colloids in the glass layer yielded a small series and contact resistance. By considering the above arguments, a percolation model has been introduced in which metallic Ag colloids generate current filaments across the glass layer. This reduces the resistivity of the glass layer and thereby introduces a percolative nature of the current via Ag nanocolloids. The percolation limit for the 2d case was calculated for periodically arranged colloids with equal size and yields a minimum volume fraction of 15% for the Ag colloids in the glass layer.

1. Introduction

For the past 30 years, considerable efforts have been made to improve the contact formation on front side silver (Ag) thick film contacts in single-crystalline silicon (Si) solar cells with n-type emitters. Screen printing is the most relevant contacting technology, due to its simplicity, cost effectiveness and high throughput.

Pastes used for front side metallization typically consist of glass frits, Ag powder, organic binders and metal oxides. Altogether more than 10 different elements are contained in a paste, it is chemically very complex. The contact formation has been reviewed by Horteis et al. [1] considering electrical properties and conduction mechanisms, microstructural features of the contact and proposing chemical reactions for contact formation that occur during the high-temperature annealing.

For contacts prepared by screen printing the contact resistance is typically in the range of a few mΩ cm^2. Such contacts do not significantly degrade the efficiency of the cell, since the series resistance remains still acceptably low. Therefore, preparing optimal contacts by screen printing has turned out to be a key for providing cost-efficient, high-efficiency solar cells. In contrast, contacts that are prepared with more advanced technologies yield a contact resistance of 10^{-5} Ω cm^2 for the same substrate [2]. Screen printed front side contacts exhibit a complex Si/Ag interface [3,4]. At this contact interface, Ag nanocrystals penetrate the Si emitter. Typically, a glass layer with thicknesses varying from a few nm up to several hundred nanometers, contains highly conductive Ag nanocolloids.

The metal–semiconductor contact interface has attracted scientific interest over decades, starting before Bardeen's paper was published in 1947 and ending today with still many unsolved questions around [5]. Fundamental basics of the metal contact relevant for solar cells are given in Refs. [6–8]. The correct understanding of Schottky barriers at metal–semiconductor

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interfaces took decades and the role of the atomic structure at the interface determining the Schottky barrier height (SBH) was realized by Tung [9,10]. It turned out that the orientation of the Si substrate plays a key role for the SBH of epitaxially deposited silicide films.

For solar cells screen printing technology it was realized late and only recently that the structure of the contact (strongly) influences its electrical properties. The paper of Ballif et al. [3] received the widest attention (cited 130 times) and is still the most frequently cited reference on this topic. Both papers the paper of Tung for epitaxially grown silicides on Si and the paper of Ballif et al. for screen printed solar cells stress the importance of the microstructure for the electrical properties of the metal–semiconductor contacts [3,9]. The paper of Ballif et al. showed microstructure of the contact down to the nm scale (by TEM). Therefore, this paper added considerable insight also for a better understanding of the electrical properties of the contact. The main question for understanding contact resistances was: where does the current flow? The essential result of Ballif et al. was that Ag nanocrystals are present at the Si surface and that authors measured a very low contact resistance of $10^{-7}\,\Omega\,cm^2$ for such nanocrystals to the emitter by conductive AFM [3]. It was then concluded that the current path would go only over such nanocrystals, preferably via direct connections to the bulk Ag. If direct connections would not be available then a "tunneling" through the glass layer was proposed. The glass layer was assumed to be insulating with a specific resistance of $10^9\,\Omega\,cm$ [3]. It is well known, however, that in oxides electrical conductivity is determined by oxygen vacancies and doping and that this assumption, therefore, is not applicable without considering the details. It is worth noting that Ballif et al. investigated (i) planar ⟨100⟩ Si surfaces and (ii) that they did not measure the contact resistance of that sample for which microstructural analysis was carried out. Rather they pointed out that contact resistance usually is in the range of $m\Omega\,cm^2$. We will show in this paper that the results of Ballif can easily be understood in a misleading way if the (i) orientation of the substrate was not considered and (ii) if contact resistance was not measured explicitly. Indeed the number of papers that combine contact resistance measurements with microstructural analysis are very few.

A number of papers were published on the topic of solar cell metallization: where does the current flow? by Kontermann and Willeke and by Pysch and Glunz [11,12]. Kontermann and Willeke obtained microscopic *I–V* measurements on individual Ag crystals on ⟨100⟩ Si and claimed contact resistances of $3\,m\Omega\,cm^2$, measured by TLM [11]. Note that in Fig. 1 [11] the Si surface appears as planar and only pyramidal shaped nanocrystals are being displayed. However, Fig. 2 clearly shows that a textured sample was used, as was also mentioned indirectly in the text [11]. The applied method of microscopic *I–V* measurements is technically complicated, can only be performed on a very small number of samples and, therefore, is not widely spread. In contrast Pysch et al. identified the role of the Si substrate orientation for forming different types of Ag nanocrystals and referred to a paper of Khadilkar et al. [12,13]. However, this important message was not received with the necessary attention by the community. It is this paper by Pysch et al. that is the right starting point for understanding the results presented here. Pysch et al. applied standard methods: (i) contact resistance measurements by TLM together with microstructural analysis and (ii) recognized the influence of the Si surface on the microstructure of the Ag nanocrystals to a first extent [12]. The main target of this paper was, however, the silver plating on a seed layer and not the screen printed contact itself. Therefore, still major questions remained to be solved for the screen printing: (i) what is the influence of the paste and (ii) what is the influence of the Si orientation on the contact resistance and (iii) where does the current flow?

In summary, two models were reported in the literature to explain the contact resistance: model I assumes that Ag crystals penetrating the Si surface represent the dominating current path, especially if they are directly connected to the Ag bulk [3,4,12]. Model II assumes that the current flows through the glass layer by Ag nanocolloids assisted tunneling [14,15], since the resistivity of the glass layer is assumed to be significantly lower with Ag nanocolloids present in the glass phase. In addition, Lin et al. suggest that the Ag colloids in the glass phase are more favorable than few Ag crystals and that they play a vital role for the transport through the glass layer across the Si/Ag interface [16].

The orientation of the Si substrate was investigated in the literature [13,17–20] and affects the shape of Ag nanocrystals, however, no explanation with respect to the electrical properties was given in these publications. Cabrera et al. observed a high contact resistance on planar ⟨100⟩ Si as compared to textured Si having (111) faces, the results were discussed in more detail in [18,21].

The existence of two models rather than one for the current path as explained above comes from the two very different Si metal interface structures of ⟨100⟩ and ⟨111⟩ oriented Si: primarily ⟨100⟩ planar contacts were studied, textured cells have ⟨111⟩ oriented surfaces yielding a different microstructure and also electrical properties. However, the differences in structural and electrical properties of planar and textured contacts have not been fully realized. Since these two contact types yield very different microstructures, as will be shown here, two models are necessary, one for ⟨100⟩ planar, the other for textured cells which are mostly related to ⟨111⟩ planar. Also the term "tunneling through the glass layer" has been used in a misleading way together with the assumption that the glass layer was insulating [3]. This will be pointed out in the discussion in more detail.

The influence of paste composition, firing process and the role of the gas atmosphere during annealing on the specific contact resistance were studied [1,4,22–26]. However, a detailed investigation of Ag nanocrystals formation on differently oriented Si substrates (planar ⟨100⟩ and ⟨111⟩) and its correlation to macroscopic electrical properties particularly the series and the contact resistance has not been systematically carried out yet.

The objective of the experimental work summarized here was to investigate the contact formation mechanism and the potential current paths from the Si emitter to the Ag bulk. For this processing of the cells was identical for all textured cells, only the front side metallization differed, an analogous procedure was used for planar cells.

A large number of cells were produced [21,27,28], their electrical properties, series and contact resistance in particular, were measured. Among these cells, few of them were selected for microstructural analysis in order to investigate the effect of the surface orientation and the paste properties on the contact resistance, because microstructural analyses require a substantial effort. The following important findings could be made: (i) the crystallographic orientation of the Si substrate and (ii) the wetting behavior of pastes strongly affect the contact microstructure and determine the contact resistance.

For investigating the orientation dependence planar cells with ⟨100⟩ and ⟨111⟩ Si orientation were processed and correlate the shape of Ag nanocrystals to the measured contact resistance [24]. Anisotropy of surface properties in Si are well established: (111) planes of Si are closed packed, and yield a small surface as well as interface energy as compared to other crystallographic planes i.e. (100). Cheek et al. reported that (111) oriented Si oxidizes three times faster as compared to (100) oriented Si [29]. Also they pointed out that the ⟨111⟩ Si has lower contact resistance than