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Influence of Si surface orientation on screen-printed Ag/Al contacts

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Abstract

In this study the influence of the crystallographic surface orientation of n-type Si wafers on the contact formation of Ag/Al thick film pastes to p^+-type Si layers is investigated. Therefore, n-type Si wafers with two different crystallographic orientations, namely polished (111) and (100) FZ wafers, with BBr_3 based emitter and 75 nm SiN_x:H are screen-printed with Ag/Al paste. Then contacts are fired in either a slow firing process or a fast one with the same peak temperature. Afterwards, contacts are prepared for scanning electron microscopy (SEM) analysis. The Ag/Al contact spots show different shapes on the differently oriented surfaces. For the slow firing process, no significant difference in number and size of the contacts spots can be found for the two surfaces. For samples fired in the fast firing process, the density and size of the contact spots on (100)-oriented surfaces is strongly reduced, whereas for the (111) surfaces only a slight reduction in density is visible as compared to the slow firing process.

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Keywords: Boron emitters; crystal orientation; metallization; p^+ Si; scanning electron microscopy (SEM); screen-printing

1. Introduction

In the production of solar cells, for different material and cell technologies differently structured surfaces have to be metalized. For pure Ag screen-printing pastes size and spatial density of Ag crystallites on the Si surface depend, among other things, on the temperature profile and the crystallographic orientation of the Si base material [1, 2]. Schubert has shown that less Ag crystals can be found on planar (100) Si wafers compared to alkaline textured surfaces [1]. Khadilkar et al. compared the Ag crystal growth of screen-printed Ag contacts on polished (100) and

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(111) FZ wafers and found more Ag crystals on (111) wafers. B doped emitters on n-type Si wafers are commonly contacted with Al containing Ag screen-printing pastes. On alkaline-textured Czochralski (Cz) wafers, these pastes feature Ag/Al contact spots grown into the Si surface that are deep enough to penetrate the emitter and therefore corrupt the space charge region [3, 4]. Frey et al. have shown that the density of the contact spots increases with rising peak temperature of the firing process [5]. In this work the influence of the crystallographic orientation of the Si wafer on the contact formation with Al containing Ag screen-printing pastes is investigated. Therefore, polished n-type FZ wafers with (111) and (100) crystallographic orientation are screen-printed and fired in two different firing processes with same peak temperature but different duration. Contacts are then analysed by means of SEM.

2. Experimental

After cleaning, a 50-60 Ω/□ BBr_3 based emitter was diffused into the wafers with different crystallographic orientation. Afterwards the borosilicate glass was removed and a 75 nm thick SiN_x:H layer with a refractive index of n=2,05 was deposited in a indirect PECVD system. Then Ag/Al paste was screen-printed on the different wafers. The samples were fired in one of two processes. The temperature profiles of the different processes are shown in Fig. 1. Samples were treated either in a single wafer process with a slow firing profile (peak temperature 800°C, measured on wafer, >14 s above 550°C) in a quartz furnace or in a standard firing process in a belt furnace (fast process, <10 s above 550°C) with the same peak temperature measured on the wafer.

All samples were prepared for subsequent SEM analysis: contacts were etched back either in HF to remove the glass layer and the bulk metal on top of the glass or in *aqua regia* to remove only the bulk metal. Additionally, for the HF etched samples FIB (focused ion beam) cross-sections of the contact spots were prepared.

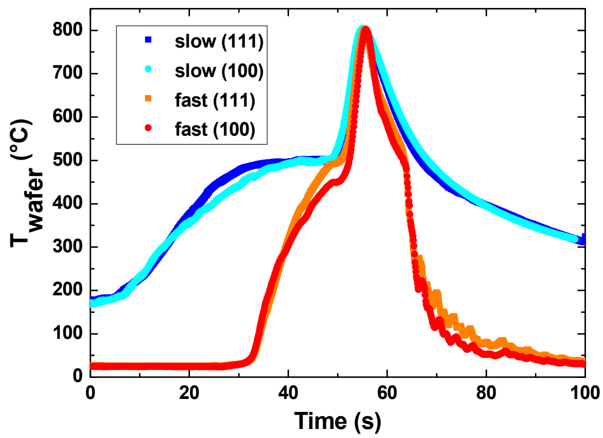

Fig. 1. Temperature profiles of the slow and the fast firing processes for both types of wafers.

3. Results

3.1. Slow firing process (single wafer process)

In Fig. 2 contacts etched back in HF are shown. On the (111)-oriented surface the Ag/Al contact spots have a triangular shape with an edge length of up to several microns ((1) in Fig. 2 a)). The contact spots on the (100)-oriented samples in contrast show the well known quadratic shape ((1) in Fig. 2 b)), with a comparable size. The Si surface close to ((2) in Fig. 2) and further away ((3) in Fig. 2) from the contact spots shows a different contrast that can be explained by a different etching behaviour of the glass frit in different regions of the contact [6]. There is no remarkable difference between the number and size of the contact spots on the samples with different crystallographic orientation.

In Fig. 3 parts of the same samples etched back in *aqua regia* can be seen. As a result of a direct contact between the bulk contact and contact spots [6], the contact spots are removed by *aqua regia* and imprints of the contact spots on the Si surface are visible in these regions (see (1) in Fig. 3). In case of the (111) surface, the Ag/Al contact spots have the shape of flat triangles ((1) in Fig. 3 a)). On the (100)-oriented Si (Fig 2b), the contact spots have the shape of inverted pyramids. The differences in glass contrast ((2) compared to (3)) are probably caused by a different glass composition and are further discussed in [6].

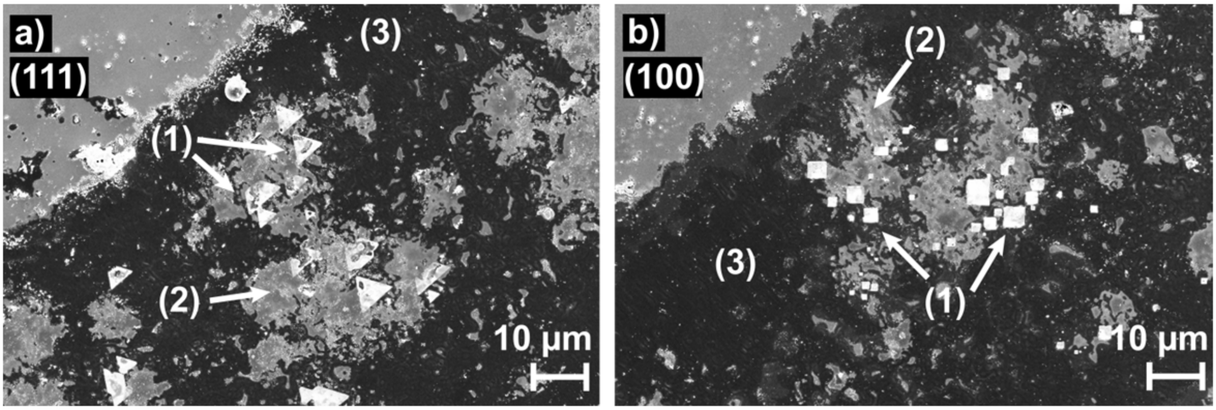

Fig. 2. SEM micrographs of samples fired in the slow firing process and etched in HF. a) (111)-oriented sample: Ag/Al contact spots show a triangular shape (1). b) (100)-oriented sample: Ag/Al contact spots show a quadratic shape (1). The surface close to (2) and away from (3) the contact spots shows a different contrast.

To analyse the depth of the contact spots, FIB cross-section were prepared (see Fig. 4). The Ag/Al triangles on the (111) surfaces show a depth of less than 1 µm (a)). In contrast to that, the inverted Si pyramids on the (100) wafers that can be seen in Fig. 4 b) penetrate several microns into the Si.

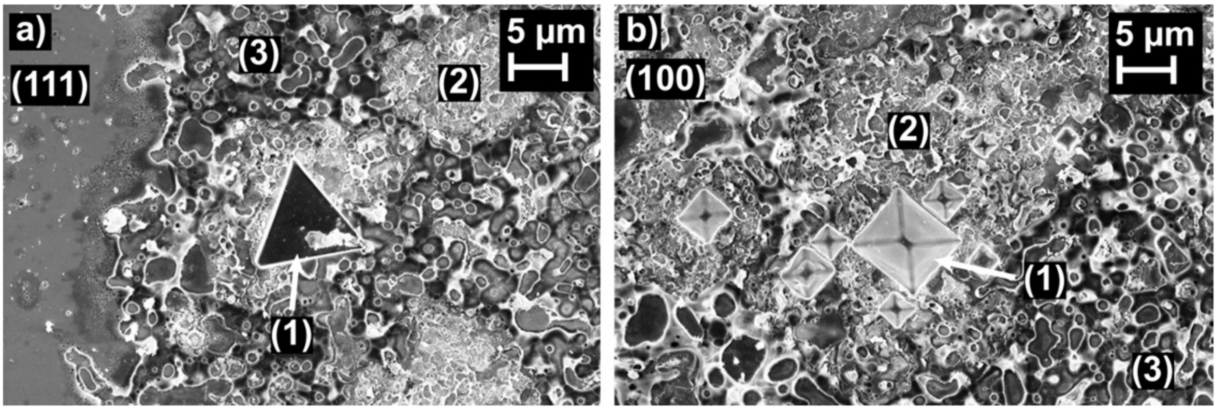

Fig. 3. SEM micrographs of samples fired in the slow firing process and etched in *aqua regia*. a) (111)-oriented sample: the imprints of the Ag/Al contact spots in the shape of flat triangles are visible (1). b) (100)-oriented sample: the imprints have the shape of inverted Si pyramids (1). The glass close to (2) and in distance to (3) the contact spots shows a different contrast probably caused by a different composition [6].

3.2. Fast firing process (belt furnace)

Fig. 5 shows SEM images of the samples fired in the fast firing process. For the (111)-oriented samples in Fig. 5 a), the density of Ag/Al contact spots is slightly reduced as compared to Fig. 2 a). The size of the triangles is comparable with the ones of the slower firing process. In contrast, for the (100)-oriented samples in Fig. 5 b), size and density of the contact spots are strongly reduced compared to the slowly fired samples. Again the difference in Si surface structure close to (2) and away from (3) the contact spots is visible.

4. Discussion

On polished (111)-oriented samples the contact spots show a flat triangular shape. They penetrate less deep into the Si material compared to the inverted pyramids on (100) surfaces. With a depth of < 1µm the risk of shunting is strongly reduced, compared to the deep inverted pyramids on (100) surfaces.

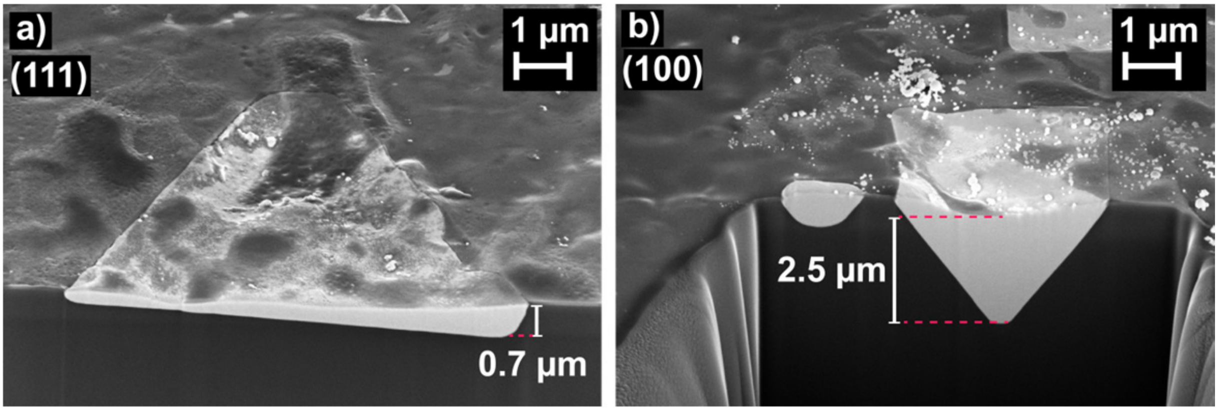

Fig. 4: FIB cross-sections of contacts fired in the slow firing process: a) the Ag/Al contacts on (111) surfaces show a flat triangular shape with a depth of < 1 µm. b) Ag/Al contact spots on (100) oriented wafers grow as inverted pyramids into the Si surface with a depth of up to several microns.

(100) samples fired in the slow firing process feature contact spots in size and spatial density comparable to (111)-oriented samples. In contrast, (100) samples prepared with the fast firing process exhibit smaller and spatially less dense contact spots than the (111) wafers. We therefore conclude that (111) surfaces can be contacted better by Ag/Al screen-printing paste in fast firing processes. Longer firing processes are necessary to reliably contact planar (100) surfaces. This is consistent with the behaviour of alkaline textured (featuring random pyramids with (111) facets) compared to NaOH etched (100) oriented Cz Si wafers, not further discussed here, where considerably less Ag/Al contact spots can be found on the (100) surfaces on the NaOH etched samples compared to the alkaline textured wafers.

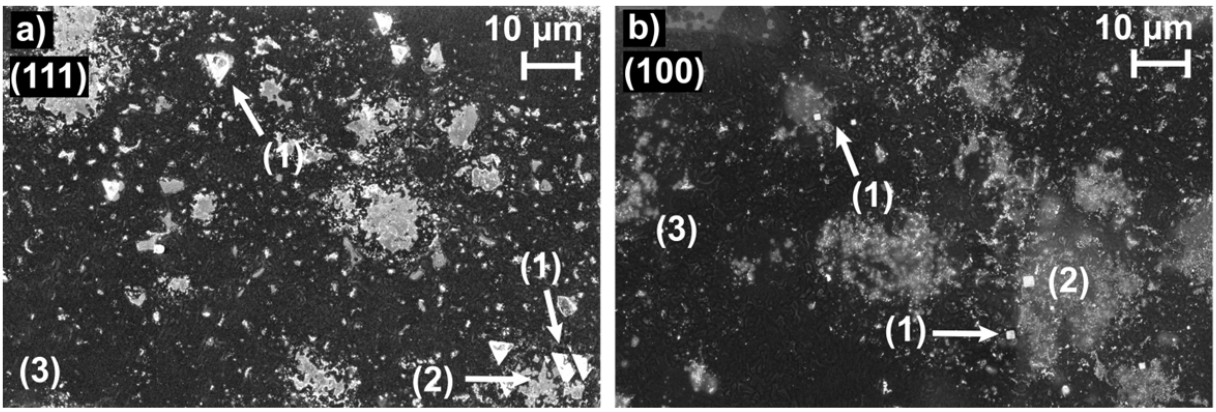

Fig. 5. SEM micrographs of samples fired in the fast firing process and etched in HF. a) (111)-oriented sample: Ag/Al triangles have a size comparable to the slow firing process (1). b) (100)-oriented sample: Ag/Al contact spots are smaller than in the slow firing process (1). The surface close to (2) and away from (3) the contact spots shows a different contrast.

To explain the observations, different approaches are conceivable:

Hilali et al. propose that the difference in the density of Ag crystals on alkaline textured and NaOH etched wafers is due to a faster etching of SiN_x on textured surfaces [7]. As in this work planar wafers are compared, this cannot be the case here.

As recently described in [8], the surface morphology of the Si wafers can influence contact formation. To exclude these effects, in this experiment wafers with the same surface morphology were chosen - polished FZ wafers were used. However, the SiN_x:H layer as well as the glass frit in the paste can influence the Si surface structure and thereby the contact formation. It is assumed, that the SiN_x:H layer grows identically on both surfaces (besides maybe the initially grown layer (few nm)) due to its amorphous character. Additionally Fritz et al. have shown that the glass frit does not etch the Si surface close to the Ag/Al contact spots [6]. The surface is protected by the residual SiN_x:H layer and shows an undamaged surface structure in these regions. Therefore, the influence of glass frit and SiN_x:H layer on the surface morphology of the Si close to the contact spots, and therefore their influence on the contact formation process should be identical for both wafer types.

Another possible explanation is that the activation energy for the growth of Ag/Al contact spots on (111)-oriented surfaces is smaller than on (100) planes [1]. So the growth of Ag/Al contact spots on (100) surfaces starts later in the firing process. In this case, the question arises why the difference in size and density of the Ag/Al contact spots that is visible after the short firing process cannot be observed any more after the longer firing process. When the temperature is high enough, contacts start to grow into the (100) plane as inverted pyramids. At the beginning of the contact formation process the inverted Ag/Al pyramids are small and therefore the Ag/Al-Si interfaces–the active interfaces where Si can be dissolved–are small as well. In the firing process the Ag/Al contacts grow. The larger the inverted pyramids get, the larger the active metal-Si interfaces get. As more Si can be solved, the contacts grow faster now. The growth of contact spots on plane (100) wafers therefore accelerates during the firing process. For the (111)-oriented wafers the interface between Si and metal does not change to this extend, as they grow mainly vertically into the Si not changing their surface size a lot. The growth rate stays uniform during the contact firing process. Therefore, the difference in size and number of Ag/Al contact spots on the different surfaces that is observable in the fast firing process is no longer visible after the slow firing process.

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