Erschienen in: Energy Procedia ; 67 (2015). - S. 43-48
https://dx.doi.org/10.1016/j.egypro.2015.03.286

ELSEVIER

CrossMark

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 67 (2015) 43 – 48

Energy
Procedia

5th Workshop on Metallization for Crystalline Silicon Solar Cells

Preservation of Si surface structure by Ag/Al contact spots – an explanatory model

Susanne Fritz[a], Stefanie Riegel[a], Axel Herguth[a],
Markus König[b], Matthias Hörteis[b], Giso Hahn[a]

[a]University of Konstanz, Department of Physics, P.O. Box 676, 78457 Konstanz, Germany
[b]Heraeus Precious Metals GmbH & Co. KG, Heraeusstr. 12 - 14, 63450 Hanau, Germany

---

Abstract

In the past years, the contact formation of Ag screen-printing pastes to n^+ emitters has been profoundly investigated and at least in parts explained. However, p^+ emitters cannot be contacted well with standard Ag pastes. It has been shown that adding Al to Ag screen printing pastes leads to lower contact resistances. Therefore different mechanisms must play a role in the contact formation process. The role of Al and the exact mechanism of contact formation of these Al containing Ag screen-printing pastes have not been well understood up to now. A drawback of Al containing pastes is that metal spikes growing into the Si wafer can be deep enough to corrupt the space charge region and contact the base thus shunting the pn-junction. A better understanding of the contact formation process is necessary to enable the development of improved screen-printing pastes with a reduced probability of shunting. In this work the influence of differently structured Si surfaces on the contact formation to a BBr_3 based boron emitter is investigated. The Ag/Al contact spots that grow into the Si surface show the same surface structure as the surrounding Si. It is concluded, that the SiN_x:H layer acts as a mould of the Si surface for the growth of the contact spots. The presented observations are then explained by a recently introduced model for the contact formation of Al containing Ag screen-printing pastes to p^+ emitters through a SiN_x:H layer.

Peer-review under the responsibility of Gunnar Schubert, Guy Beaucarne and Jaap Hoornstra

Keywords: metallization, srcreen printing, boron emitter, SEM, surface structure

---

1. Introduction

In the past years, contacting n^+ emitters with Ag screen-printing pastes has been the topic of many investigations [1,2] and the contact formation process has been understood to a large extend. Good quality electrical contacts are obtained with Ag pastes on n^+ emitters with specific contact resistances below 5 mΩcm². In contrast p^+ emitters cannot be contacted well with standard Ag pastes [3-6] and contact resistances for samples similar to the ones examined in this study are above 20 mΩcm². The specific contact resistance of Ag screen-printing pastes to

Peer-review under the responsibility of Gunnar Schubert, Guy Beaucarne and Jaap Hoornstra
doi:10.1016/j.egypro.2015.03.286

p^+ emitters can be lowered by adding Al to the paste [3-6]. For these pastes different mechanisms must play role in the contact formation process which has not been well understood up to now. With the addition of Al a new problem arises. Ag/Al contact spots that grow into the Si surface can be deeper than 1 µm and therefore penetrate the emitter and corrupt the space charge region or shunt the pn-junction. Further investigations of the contact formation process and the spiking problem can help to solve this problem and to establish better screen-printing pastes for p^+ emitters. In this investigation samples with different surface structures are contacted with Al containing Ag screen printing paste. A SEM and EDX analysis of the differently prepared samples is conducted to gain deeper insight into the contact formation process of Al containing Ag screen-printing pastes.

2. Experimental

N-type Cz-Si wafers with a resistivity of ≈ 3 Ωcm were strucutred by alkaline, plasma and iso-texture to obtain different surface structures. Afterwards, in a BBr_3 based diffusion a boron emitter with a sheet resistance of ≈ 50 Ω/□ and a boron surface concentration of $N_{surface} \approx 3 \cdot 10^{19}$ cm^{-3} was formed. The removal of the borosilicate glass was followed by the deposition of 75 nm SiN_x:H in a plasma-enhanced chemical vapour deposition (PECVD) process. In the following transfer length method (TLM) test structures with a finger width of 200 µm and varying finger distance were screen-printed on the differently structured wafers with an Al containing Ag screen-printing paste. The wafers were fired in a belt furnace. The temperature profiles for the different samples were adapted to reach a peak sample temperature of ≈ 800°C.

Contact resistance was determined using TLM. Afterwards, samples were cut into pieces to prepare them in different ways for subsequent SEM (scanning electron microscopy) and EDX (electron dispersive X-ray) analysis: for top-view analysis, samples where etched either in hydrofluoric acid (HF, 5%) to remove the glass layer and the bulk metal on top of this layer, or in *aqua regia* to remove only the bulk metal. To obtain cross-sectional information, samples were embedded in epoxy resin and mechanically polished to allow an analysis the whole contact cross-section.

3. Results

The specific contact resistance ϱ_c of the samples is shown in Table 1. The lowest ϱ_c of 2.45 ± 0.84 mΩcm² was found for plasma textured samples. The reduced contact resistance for this surface is due to a higher density of Ag/Al contact spots on the Si surface [7,8] what is confirmed by SEM analysis.

Table 1: Specific contact resistance ϱ_c for different surface structures

Surface structure	ϱ_c (mΩcm²)
Alkaline textured	4.8 ± 0.3
Plasma texture	2.45 ± 0.84
Iso-textured	21.26 ± 2.15

In Fig. 1 SEM micrographs of the samples etched in HF can be seen. The Ag/Al contact spots (1) that have grown into the Si surface can be distinguished from the surrounding Si. The surface shape of the contact spots is identical to the shape of the surrounding Si surface for all three textures: for the alkaline textured samples the contact spots show the pyramidal structure of the Si (a), on the plasma textured samples the small holes of the nano-texture are visible on the contact spots (b) and the sharp edges of the iso-textured surface are reproduced as well (c).In [7] it was reported, that the Si surface is etched by the glass frit in distance to the Ag/Al contact spots, but not close to them. The same can be observed for the samples in this experiment as can be seen in Fig. 1. Close to the contact spots the Si surface is not corroded (2), away from them it is etched by the glass (3). Especially for the plasma texture (b) the difference in the Si structure close to and away from the contact spots is obvious.

The samples etched in *aqua regia* are shown in Fig. 2. On all samples the glass layer is interrupted by inverted Si pyramids (1) as previously reported for alkaline textured surfaces [9]. The two different glass regions described there can as well be seen on the three samples. Around the openings in the glass layer the glass looks bright and the Si surface structure can be seen through the layer (2). With EDX measurements the presence of Al and N in these regions is confirmed for all surfaces. Away from the contacts spots the glass is dark and seems to be thicker (3) as the Si surface structure is not visible. Here no Al and N can be found.

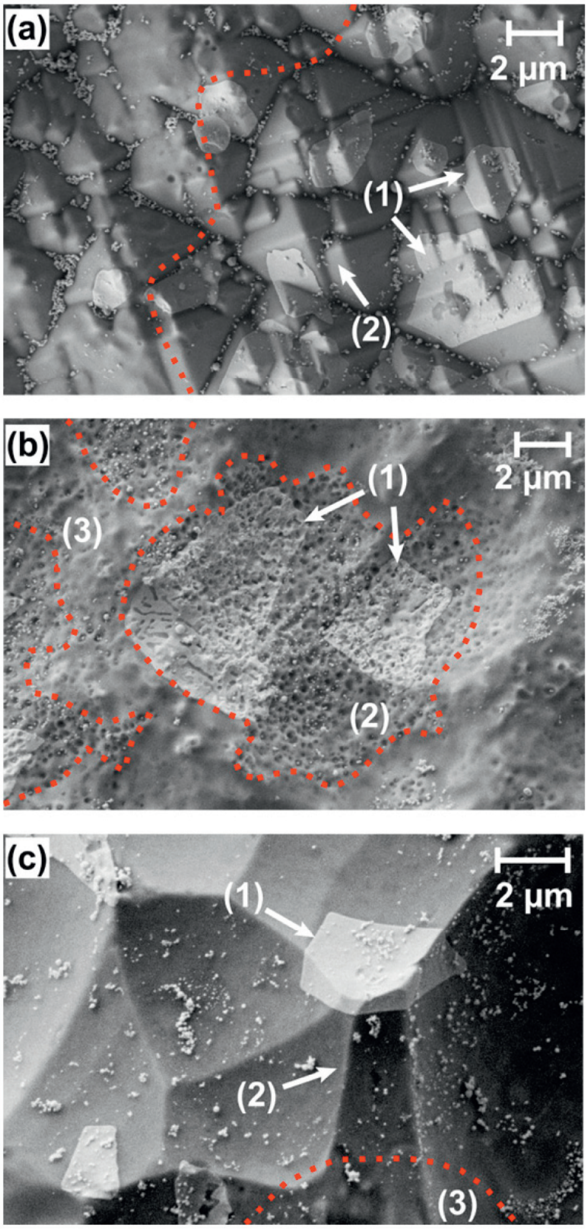

Fig. 1. SEM micrographs of differently textured samples etched in HF: (a) alkaline, (b) plasma and (c) iso-texture. The Ag/Al contact spots (1) are surrounded by an intact Si surface (2) that is not etched by the glass frit. Away from the contact spots the Si surface is corroded by the glass frit (3).

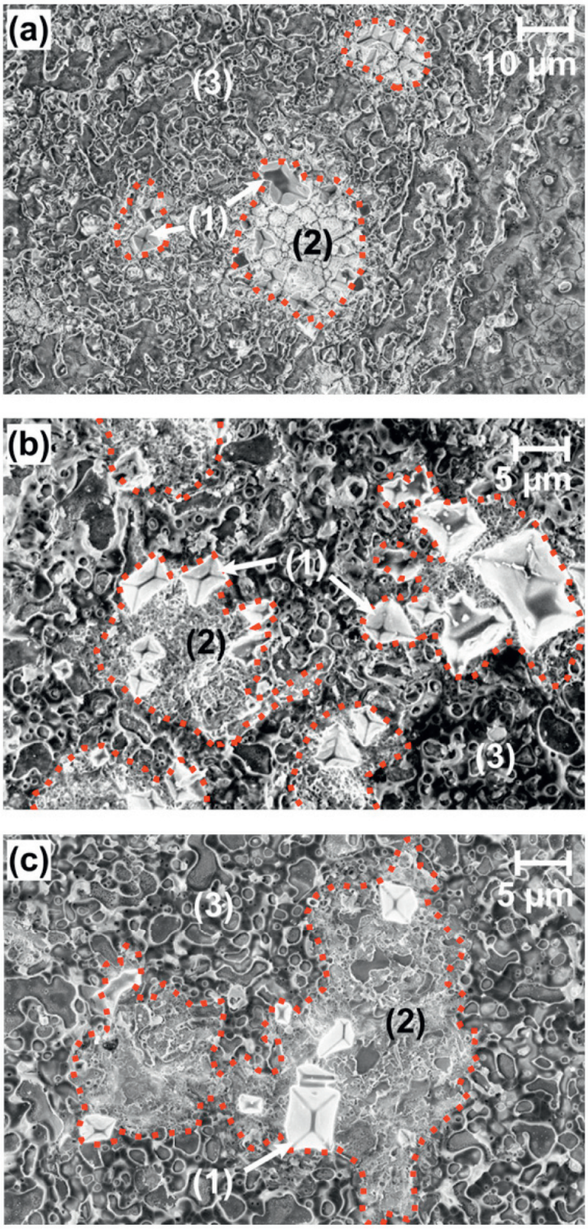

Fig. 2. SEM micrographs of differently textured samples etched in *aqua regia*: (a) alkaline, (b) plasma and (c) iso-texture. Around the inverted Si pyramids (1) the glass layer is bright and Al and N can be detected. Away from the contact spots the glass looks darker (3). No N and Al can be found here.

For further investigating the reason for the preservation of the Si surface structure by the Ag/Al contact spots, cross-sections of the contacts were analyzed by SEM (see Fig. 3). Contact spots (1) grow below parts of the contact with an inhomogeneous microstructure (2) [7]. This part of the contact consists of an Ag/Al phase and Al containing glass. The part of the contact without Al shows a homogenous microstructure (3). The thin layer between the Ag/Al contact spot and the bulk contact (4) is visible for all samples. N can be detected in this layer marked by the red crosses. The circles around the crosses indicate the excitation region of the electron beam. The thickness of the layer is up to around 80 nm. Especially in (a) the adaption of the Si surface structure by the Ag/Al contact spots can be seen. There are also contact spots where no interface layer is visible. In (a) additionally Si residues (5) can be seen above the contact spot. These Si residues can also be observed above several contact spots of the other samples not shown here. Between the Al containing part of the contact and the Si surface N can be detected as well [7].

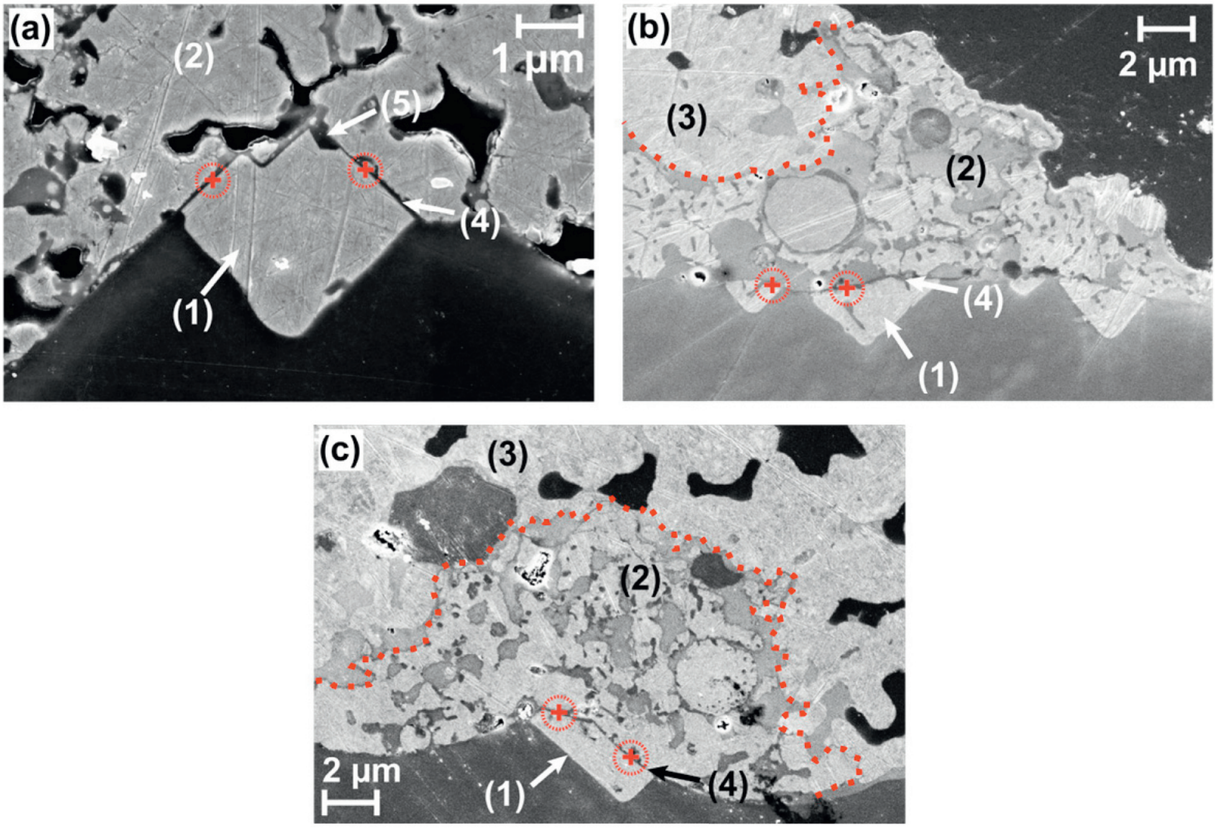

Fig. 3. Polished cross-sections of the samples with different surface structure: (a) alkaline texture, (b) plasma texture, (c) iso-texture. Above the Ag/Al contact spots (1) the contact has an inhomogeneous microstructure (2) and contains Al, compared to the homogenous microstructure (3) without Al. Between the contact spots and the contact a thin layer is visible (4), here N can be detected (crosses).

4. Discussion

To make sure that a reasonable electrical contact was formed on all surfaces the specific contact resistance ϱ_c of the different samples was measured (see Table 1). For plasma textured samples the lowest ϱ_c is found. This low value was attributed to a high density of Ag/Al contact spots on the Si surface in accordance to SEM micrographs. As the thickness of the SiN_x:H layer as well as the coupling of the thermal energy into the wafer in the firing process depends on the surface structure, it cannot be concluded that an iso-textured surface can be worse contacted by Ag/Al screen-printing pastes in all cases.

For all textures the Si surface structure is preserved by the Ag/Al contact spots: the sharp edges of the alkaline and iso-textured surfaces as well as the small holes of the plasma structured sample are reproduced (Fig. 1). Additionally, close to the contact spots the Si surface remains unaffected regarding etching by the glass frit although away from the spots the Si surface is corroded. The regions with the intact Si surface structure (Fig. 1 (2)) are covered by the bright glass that can be seen in Fig. 2 (2). N and Al are detected here. These observations lead to the assumption that the Si surface is protected by a layer that prevents the etching of the Si by the glass frit. Furthermore, this layer acts as a mould for the surface of the Ag/Al contact spots.

N could be found in a thin layer between the Al containing part of the contact and the Si surface as well as between the bulk contact and the contact spots [7]. It was concluded that this N originates from a residual SiN_x:H layer that protects the Si surface around the contact spots from being etched by the glass frit. The maximal thickness of the interface layer of ≈ 80 nm gives a further hint for this conclusion. In the present study it is confirmed that this behavior is valid for various surface structures. N as well as Si residues can be found above the contact spots.

The observations made can be explained by the model for contact formation for Al containing Ag screen-printing pastes by Fritz et al [7]: Ag/Al contact spots grow through holes in the residual SiN_x:H layer. As the layer remains, the spots then expand below this layer. When the Ag/Al phase reaches the SiN_x:H layer the growth in this direction stops. As the layer was deposited on the Si surface, it presents a mould of the structure of the surface. Therefore, the surface of the Ag/Al contact spots adopts the shape of the SiN_x:H mould and thus the shape of the former Si surface. As the mould covers most of the Si surface below the Al containing part of the contact, the Si surface is protected in these regions and the Si surface structure remains unaffected by the glass frit as can be observed in Fig. 1 (2). When the expansion of the Ag/Al contact spots does not reach the SiN_x:H layer during the heating of the samples, part of the Si surface remains between the mould and the contact spots as can be seen in Fig. 3 ((a)(5)). Additionally, the residual SiN_x:H layer protects the Si surface below the inhomogeneous, Al-containing parts of the contact. Therefore, the surface is not etched by the glass frit and an intact Si texture can be observed in these regions on the SEM images for the different surface structures.

5. Conclusion

In this study a SEM analysis of Ag/Al screen-printed contacts on Si wafers exhibiting different surface structures was conducted. The Ag/Al contact spots grown into the Si surface show the same surface structure as the surrounding Si surface. Additionally, the Si surface surrounding the contact spots is unaffected by the etching of the glass frit. A cross-sectional examination of the contacts shows a thin layer containing N covering the Ag/Al contact spots and the Si surface around them. The layer is supposed to be a residual SiN_x:H layer. The preservation of the Si surface structure by the Ag/Al contact spots can be explained with the help of a model for the contact formation process recently presented [7]: contact spots grow through holes in a residual SiN_x:H layer. This SiN_x:H layer acts as a mould for the growth of the contact spots as the contact spots expand below the mould and stop growing there. Additionally, the mould protects the Si surface around the contact spots from being corroded by the glass frit. The presented study therefore confirms the proposed model for the contact formation process of Al containing Ag screen-printing pastes.

Acknowledgements

Part of this work was financially supported by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (FKZ 0325581) and within den KONSENS project (FKZ 0325426). The content is the responsibility of the authors.

References

[1] Ballif C, Huljić DM, Willeke G, Hessler-Wyser A. Silver thick-film contacts on highly doped n-type silicon emitters: structural and electronic properties of the interface. Appl Phys Lett 2003;82:1878-81.

[2] Schubert G. Thick film metallization of crystalline silicon solar cells: mechanisms, models and applications. PhD thesis, University of Konstanz; 2006.

[3] Lago R, Pérezl L, Kerp H, Freire I, Hoces I, Azkona N, Recart F, Jiméno JC. Screen printing metallization of boron emitters. Progr Photovolt: Res Appl 2010;18:20-7.

[4] Kerp H, Kim S, Lago R, Recart F, Freire I, Pérez L, Albertsen K., Jiméno JC, Shaikh A. Development of screen printable contacts for p^+ emitters in bifacial solar cells. Proc. 21st EU PVSEC Dresden, 2006, p. 892-4.

[5] Kopecek R, Buck T, Libal J, Petres R, Röver I, Wambach K, Kinderman R, Geerligs LJ, Fath P. Large area n-type multicrystalline silicon solar cells with B-emitter: efficiencies exceeding 14%. Proc. 15th IPSEC, Shanghai, 2005, p. 883-4.

[6] Riegel S, Mutter F, Hahn G, Terheiden B. Contact formation in the silver/aluminum thick film firing process – a phenomenological approach. Proc. 25th EU PVSEC, Valencia, 2010, p. 2353-6.

[7] Fritz S, König M, Riegel S, Herguth A, Hörteis M, Hahn G. Formation of Ag/Al screen-printing contacts on B emitters, IEEE J Photovolt, accepted for publication.

[8] Seyedmohammadi S, Graddy E, Shaik A. Screen printable Ag-Al metal pastes for p^+ silicon application in solar cells, *Proc. 35th IEEE PVSC Honolulu,* 2010, p. 3600-3.

[9] Fritz S, Riegel S, Herguth A, König M, Hörteis M, Hahn G. A phenomenological model for the contact formation of Ag/Al screen-printing pastes through SiN_x:H layers, Proc. 29st EU PVSEC, Amsterdam, 2014, in press.