A PHENOMENOLOGICAL MODEL FOR THE CONTACT FORMATION OF Ag/Al SCREEN-PRINTING PASTES THROUGH SiN_X:H LAYERS

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ABSTRACT: The process of contact formation of Al containing Ag screen-printing pastes to p^+ emitters is investigated by an electron microscopic analysis of etched-back contacts (*aqua regia* and hydrofluoric acid) and polished contact cross-sections. Ag/Al contact spots grown into the Si surface are detected below inhomogeneously structured areas of the bulk contact that contain Al. In addition, Si accumulations are found in the Ag/Al phase in these parts of the contact after contact formation. It is concluded that during the firing process Ag and Al are transported from the bulk contact to the Si surface, where Ag/Al contact spots grow. The solved Si diffuses in the parts of the contact containing Al. Despite the diffusion of Si, Ag and Al, the SiN_x:H layer below the inhomogeneous part of the contact and especially above the Ag/Al contact spots is not completely etched away, as is shown by EDX measurements using top view and cross-sectional samples. Based on the observations made by SEM and EDX analysis, a phenomenological model for the exchange of Si, Ag and Al through holes in the SiN_x:H layer and the growth of Ag/Al contact spots below the SiN_x:H layer is presented.
Keywords: p^+ Si, boron emitter, metallization, screen-printing, contact formation, SEM

1 INTRODUCTION

In the last year the interest in contacting p^+ surfaces with screen-printing has grown, as good quality contacts are needed for n-type, bifacial and back contact solar cells. The contact formation of Ag screen printing pastes to phosphorous doped, n-type Si emitters has been topic of many investigations published up to now (e.g. [1,2]). In contrast, the process of contacting p^+ Si is not yet well understood. Contacting p^+ Si with Ag screen-printing pastes that are used for contacting n^{+-} Si can lead to specific contact resistances ϱ_c above 50 mΩcm^2 [3-6]. It has been shown that adding Al to an Ag thick film paste reduces the specific contact resistance ϱ_c [3-5]. The reason for this improvement of electrical contact quality is content of ongoing research.

A drawback of Al containing pastes is that the metal spikes that grow into the Si wafer can be deep enough to corrupt the space charge region and eventually contact the base thus shunting the pn-junction [3,4].

To solve this problem and improve screen-printing pastes for contacting p^+ emitters, a better understanding of the contact formation process of Al containing Ag screen-printing pastes is necessary.

In this work the contact formation process of Al containing Ag screen-printing pastes to wafers with BBr_3 based B emitters and SiN_x:H anti-reflection layer is examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Etched-back contacts and cross-sections of the contact fingers are compared to gain deeper insights in the morphology of the contact and the process of contact formation.

2 EXPERIMENTAL

For the experiment n-type Cz-Si wafers with a resistivity of ~3 Ωcm were textured in an alkaline bath resulting in a random pyramid structure. A boron doped emitter with a sheet resistivity of 50 $\Omega/\square$ and a boron surface concentration of $N_{surface}$~$3\cdot10^{19}$ cm^{-3} was formed within a BBr_3 based diffusion in a tube furnace. After removing the borosilicate glass a ~75 nm thick PECVD (plasma enhanced chemical vapour deposition) SiN_x:H layer was deposited. Contact formation of the Al containing Ag screen-printing paste was realized by printing a test structure with a finger width of 200 µm and firing under standard conditions in a belt furnace (peak temperature ~800°C). For subsequent SEM and EDX analysis of the contact area samples are either etched back in *aqua regia* (HNO_3:HCl, 1:3) to remove the bulk metal only, or in hydrofluoric acid (HF, 5%) to remove the glass layer as well. Additionally, samples are embedded in epoxy resin and polished to allow a cross-sectional SEM analysis of the contacts.

3 RESULTS

In this work, the entire contact finger is referred to as contact or bulk contact, the microscopic Ag/Al contacts (~1-5 µm) at the Si surface are called contact spots.

In Fig. 1 a SEM micrograph of a sample etched back in HF is shown. The Si surface is interrupted by white pyramids (1), which are identified by EDX measurements as Ag/Al contact spots grown into the Si surface. Around

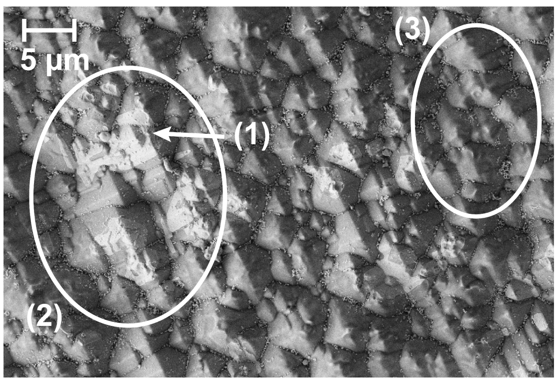

Figure 1: SEM micrograph of a sample etched in HF. Next to the Ag/Al contact spots (1) the pyramids show sharp edges (2). This indicates that they are not etched by the glass frit. Further away from the contact spots the pyramids are rounded by the glass frit (3).

the contact spots the Si pyramids are sharp edged (2), indicating that they are not corroded by the glass frit contained in the screen-printing paste. Further away from the contact spots the pyramids are rounded as a result of the etching by the glass frit (3).

The contacts etched back in *aqua regia* reveal a glass layer interrupted by Si spots with the shape of inverted pyramids (see Fig. 2, (1)). These spots correspond to the Ag/Al contact spots on the HF etched samples. Two different glass compositions can be distinguished with the SEM in-lens detector. Close to the contact spots the glass has a bright and less structured appearance (2). EDX measurements show the presence of N and Al (see EDX spectrum Fig. 2, (2)). Further away from the contact spots the glass appears darker and no N and Al can be detected (3).

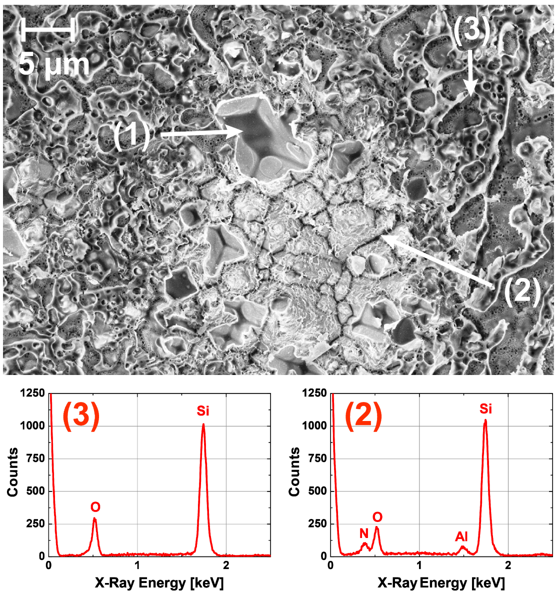

Figure 2: SEM micrograph of sample etched in *aqua regia* and EDX spectra. Si spots in shape of inverted pyramids (1) are surrounded by bright glass areas (2) where N and Al can be detected by EDX measurements. The dark regions (3), further away from the Si spots do not feature significant amounts of N.

To gain more information about the entire contact, polished cross-sections were prepared and analysed by SEM and EDX. In Fig. 3 two different regions of the bulk contact can be distinguished. The parts of the contact with a homogeneous microstructure (1) contain intact Al particles (2) or no Al and a pure Ag phase (3). In the parts of the contact where Al particles are molten (4) the contact shows an inhomogeneous microstructure (5) with an Ag/Al phase (6) and Al containing glass (7).

In Fig. 4 a contact-Si interface is shown. Ag/Al contact spots (1) are located below the inhomogeneous parts of the contact that contain Al (2). N, most probably originating from the SiN_x:H layer, can be detected between the inhomogeneous part of the contact and the Si surface as well as in a thin layer between the Ag/Al contact spots and the bulk contact (crosses). In regions, where the contact structure is homogeneous (3), no N is detected between the contact and the Si (points) and no contact spots can be found at the Si surface.

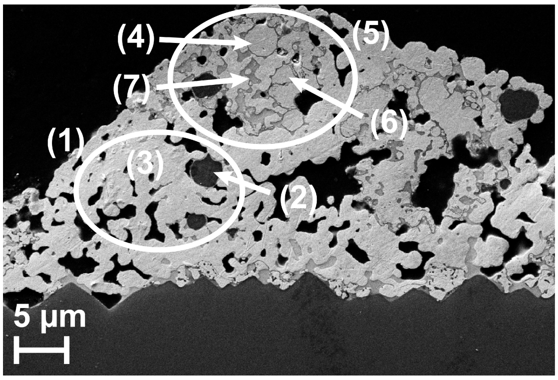

Figure 3: Cross-section of a screen-printed Al/Ag contact. In the homogeneous regions of the contact (1) only intact Al particles (2) or no Al can be found. The pure Ag phase (2) is interrupted by pores. In the part of the contact with an inhomogeneous microstructure (5) most Al particles are molten (4). This parts of the contact consist of a Ag/Al phase (6) and Al containing glass (7).

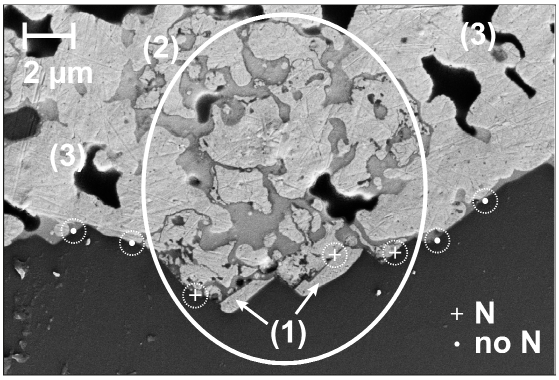

Figure 4: Cross-section of a screen-printed contact. Above the Ag/Al contact spots (1) the contact morphology is inhomogeneous (2). Below homogeneous parts of the contact (3), no contact spots can be found. The symbols show where N is detected by EDX (crosses) and where not (points). The dashed circles estimate the excitation region of the electron beam for EDX measurements.

As the Ag/Al contact spots grow into the former Si surface, the question arises where the Si remains. To answer this question, a closer look into the inhomogeneously structured parts of the bulk contact above Ag/Al contact spots is required. This is presented in Fig. 5, where another cross-section of a contact is shown. Above the Ag/Al contact spots (1) the contact shows the inhomogeneous microstructure (2) discussed before. In the Ag/Al phase dark lines and spots can be distinguished (3). EDX measurements show that these regions contain a large amount of Si. The Ag/Al phase around these Si spots is almost free of Si. In addition, in Fig. 5 the layer containing N between the contact spot and the bulk finger can be seen (4). Above the right contact spot this layer is interrupted (5) exhibiting a direct connection between the bulk finger and the contact spot.

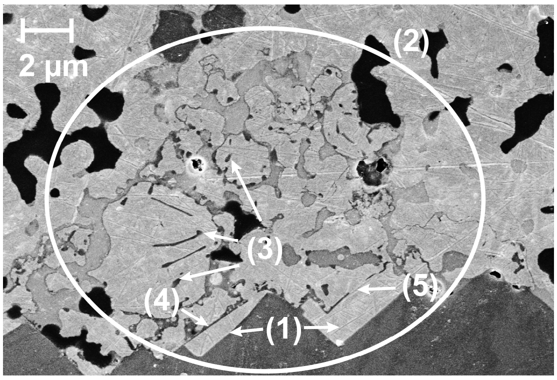

Figure 5: Cross-section of screen-printed contact. The Ag/Al contact spots (1) are located below an inhomogeneously structured part of the contact (2). The dark stripes (1) and small spots in the Ag/Al phase contain Si.

4 DISCUSSION

During the firing process Ag/Al contact spots grow into the Si surface (Fig. 1, (1)). These Ag/Al contact spots (Fig. 4, (1)) form below areas of the bulk contact that show an inhomogeneous microstructure containing Al (Fig. 4, (2)). In a thin layer between this inhomogeneous contact and the Si surface N can be detected. This N most likely originates from the SiN_x:H layer which is probably not completely etched away by the glass frit in these areas. This assumption is supported by the SEM images in Fig. 1 and 2. The Ag/Al contact spots in Fig. 1 (1) correspond to the inverted pyramids that can be seen in Fig. 2 (1). In Fig. 1 an undamaged Si surface next to the Ag/Al contact spots, probably protected by the SiN_x:H layer, is visible (2). Residues of this layer can be found in the corresponding regions in Fig. 2 (2), where N is detected. Further away from the contact spots the Si surface is corroded by the glass frit (Fig. 1, (3)). In these regions the protecting SiN_x:H layer is etched away by the glass frit, on the sample etched back in *aqua regia* no N can be found there (Fig. 2, (3)).

Additionally, SiN_x:H residues can be found in a thin layer on top of the Ag/Al contact spots (Fig. 4). In Fig. 5 (5) a hole in this N containing layer, and therefore a direct connection between the Ag/Al contact spot and the bulk metal, can be seen. The transport of Si from the Si surface into the bulk contact as well as of Ag/Al from the contact to the Si surface can only take place through these holes in the SiN_x:H layer.

In Fig. 5 it can be seen that Si segregates in the Ag/Al phase in the inhomogeneous part of the finger. During the firing process Ag/Al contact spots grow into the Si surface and Si is solved there. The Si diffuses into the inhomogeneous part of the contact where it can precipitate during the cool down.

Based on these observations a model for the contact formation process through a SiN_x:H layer is proposed (see Fig. 6).

a) Before the firing process, the contact shows a porous structure with voids, intact Al particles and Ag. The SiN_x:H layer is intact below the whole screen-printing finger.
b) At temperatures above 660°C the Al particles melt. They dissolve the surrounding Ag forming an Ag/Al phase and mix with the glass. The glass already etches the SiN_x:H layer.
c) The SiN_x:H next to the inhomogeneous region is etched away by the glass and below the inhomogeneous part a hole in the SiN_x:H layer forms.
d) Si diffuses from the volume at the Si surface where the Ag/Al contact spot forms into the bulk finger and Ag and Al grow into the Si.
e) Ag/Al contact spots grow further below the SiN_x:H layer.
f) During cooling Si accumulates in small spots and stripes in the Ag/Al phase of the inhomogeneously structured part of the contact. Finally, the Ag/Al contact is grown as an inverted pyramid in the Si surface.

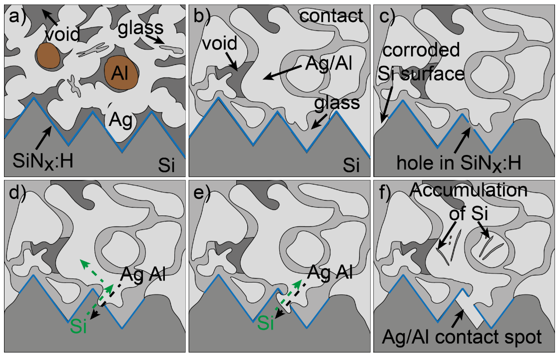

Figure 6: Proposed sequence of the formation of Ag/Al contact spots below the SiN_x:H layer.

5 CONCLUSION

In context of this work a SEM and EDX analysis of contacts of an Al containing Ag screen-printing paste on a BBr_3 based B emitter has been conducted. The observations lead to a model for contact formation. At temperatures above 660°C Al particles in the paste melt. They mix with the glass frit and dissolve the surrounding Ag forming an Ag/Al phase and an inhomogeneous microstructure. In regions where the Ag/Al phase of the bulk finger gets in contact with the Si surface, an exchange of Ag and Al from the contact into the Si surface and of Si from the Si surface into the bulk contact occurs. As the SiN_x:H layer is not completely etched away below the Al containing part of the contact, the material exchange occurs through holes in the SiN_x:H layer. As a result Ag/Al contact spots grow into the Si below the SiN_x:H layer.

6 ACKNOWLEDGEMENTS

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REFERENCES

[1] C. Ballif, D. M. Huljić, G. Willeke, A. Hessler-Wyser, Silver thick-film contacts on highly doped n-type silicon emitters: structural and electronic properties of the interface, Applied Physics Letters 82 (2003) 1878-1881.

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

[3] R. Kopecek, T. Buck, J. Libal, R. Petres, I. Röver, K. Wambach, R. Kinderman, L.J. Geerligs, P. Fath, Large area n-type multicrystalline silicon solar cells with B-emitter: efficiencies exceeding 14%, Proceedings of the15th IPSEC, Shanghai 2005, 892-894.

[4] R. Lago, L. Pérez, H. Kerp, L. Freire, I. Hoces, N. Azkona, F. Recart, J.C. Jimeno, Screen printing metallization of boron emitters, Progress in Photovoltaics: Research and Applications 18 (2010) 20-27.

[5] H. Kerp, S. Kim, R. Lago, F. Recart, I. Freire, L. Pérez, K. Albertsen, J. C. Jiméno,A. Shaikh, Development of screen printable contacts for p^+ emitters in bifacial solar cells, Proc. 21st EU PVSEC, Dresden 2006, 892-894.

[6] S. Riegel, F. Mutter, G. Hahn, B. Terheiden, Contact formation in the silver/aluminum thick film firing process – a phenomenological approach, Proc. 25th EU PVSEC, Valencia 2010, 2353-2356.