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Influence of the dopant on the contact formation to p⁺-type silicon

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Abstract

In this contribution we investigate the influence of the doping element on the contact formation to p⁺-type Si. Contacting B doped layers with Ag thick film paste leads to very few Ag crystallites at the contact interface and results in poor contact resistances [1-3]. Using Ag/Al thick film paste for contact formation, the contact is not only formed by Ag crystallites, but by diversely shaped Ag/Al contact spots and the contact resistance is reduced by more than one order of magnitude [2]. Al melting at the Si wafer surface forms Al doped rectangles on the Si wafer where the growth of Ag/Al/Pb spikes is enhanced.

When contacting Al doped layers with Ag thick film paste a larger number of Ag crystallites is observed than for B doped layers. If the contact is formed with Ag/Al paste the number of Al-rich rectangles is enhanced and we detect higher doped areas under the contact spots. The contacts detected have an ellipsoidal, pyramidal or "L-formed" shape. We conclude that not only the acceptor impurity concentration under the contact area is crucial for the contact formation, but also the properties of the specific acceptor present.

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1. Introduction

Using Ag pastes for contacting B diffused samples, the main problems during contact formation are high contact resistances (R_c) due to the depletion zone and an increased saturation current (j_{0e}) [2]. It is assumed [3], that the contact formation to p⁺-Si layers is dominated by Ag crystallites as shown for n⁺ layers [4]. By adding aluminum to this Ag thick film paste the specific contact resistance can be reduced.

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Additionally, the amount of crystallites contacting the wafer is increased [1-3]. In previous work [2] we showed, that the Al melting at the B-doped Si wafer surface forms Al doped regions on the Si wafer. In these Al doped areas the growth of Ag/Al/Pb spikes is enhanced [2]. In this work we investigate the influence of the dopant used to create the highly p-doped layer. We investigate three groups: 1) lowly B doped wafers ($N_{\text{surface}} \sim 7\text{E}15 \text{ cm}^{-3}$), 2) highly B doped wafers ($N_{\text{surface}} \sim 9\text{E}18 \text{ cm}^{-3}$), 3) highly Al doped wafers ($N_{\text{surface}} \sim 4\text{E}18 \text{ cm}^{-3}$).

2. Experimental

For sample preparation <100> oriented Cz-Si p-type wafers of $\sim 2 \Omega\text{cm}$ resistivity are used. After saw damage removal in hot NaOH_{aq} (23%, 80°C) the p^+ region is formed via BBr_3 diffusion or via screen printing and firing of Al thick film paste. The BBr_3 diffusion results in a sheet resistivity of $60 \Omega/\square$ ($N_{\text{peak}} \sim 3\text{E}19 \text{ cm}^{-3}$, $N_{\text{surface}} \sim 9\text{E}18 \text{ cm}^{-3}$). The screen printed Al thick film paste is fired in a standard firing step. The redundant Al thick film paste is removed in aqueous HCl (37%) and HF (5%) solutions. The sheet resistivity of the Al doped layer is $\sim 15 \Omega/\square$ ($N_{\text{peak}} \sim 8\text{E}18 \text{ cm}^{-3}$, $N_{\text{surface}} \sim 3\text{E}18 \text{ cm}^{-3}$). No antireflection coating is used. Contact formation with commercial Ag (2 pastes) and Ag/Al thick film paste (Al content below 5%; 5 pastes) is done via screen printing a finger grid and firing. Identical temperature profiles are used for firing of Ag and Ag/Al thick film paste. Wafer peak temperatures are 625°C and 710°C. The specific contact resistance R_C is obtained using the transfer length method (TLM). For scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) surface and interface analysis (Zeiss Neon40EsB) of the contact areas the Ag and Ag/Al contacts are removed in aqueous solution of HF (5%) as well as $\text{NH}_3:\text{H}_2\text{O}_2$ (1:1). The acceptor impurity profiles are determined by electrochemical capacitance voltage (ECV) measurement (WEP Wafer Profiler CVP21).

To exclude the influence of the wafer surface two additional Al doped groups are prepared. The wafer surface of group II is chemically polished (CP) after the removal of the aluminum paste using a mixture of HNO_3 , HF and $\text{C}_2\text{H}_4\text{O}_2$. The wafer surface of group III is etched in hot NaOH_{aq} (23%, 80°C) after the removal of the Al paste. For both groups 3 μm are removed from the surface. This results in a sheet resistivity of $300 \Omega/\square$ ($N_{\text{peak}} = N_{\text{surface}} \sim 2.3\text{E}18 \text{ cm}^{-3}$). The samples referred to as group I did not see a wet chemical treatment after the removal of the aluminum paste. The doping profiles are shown in Fig. 1.

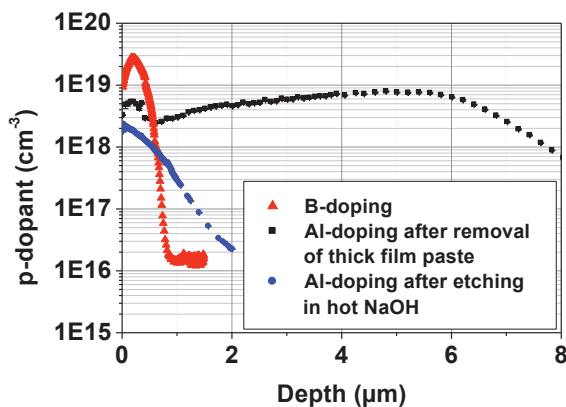


Fig. 2. Doping profiles of the contacted emitters. The profiles are determined by ECV measurement (WEP Wafer Profiler CVP21).

3. Results

3.1. Doping with boron

High doping (surface doping $\sim 9E18 \text{ cm}^{-3}$)

Earlier work showed that the specific contact resistance to p^+ Si can be reduced from 58-128 $\text{m}\Omega\text{cm}^2$ down to 0.7-7 $\text{m}\Omega\text{cm}^2$ by using Ag/Al instead of Ag thick film paste [1-3,5].

Al melting at the Si wafer surface forms Al doped regions on the silicon wafer. In these Al doped areas the growth of Ag/Al/Pb spikes is enhanced. Additionally, Al precipitates at the wafer/paste interface. The contact formation is highly dependent on the local paste composition resulting in a locally varying shape of the contact spots. Contact spot size is $\sim 0.5\text{-}10 \mu\text{m}$ ($T_{\text{wafer}} = 710^\circ\text{C}$). For more details see [2].

Further on we observed precipitates at the wafer / Ag/Al-paste interface (see orange oval in Fig. 2a). These precipitates are approximately 70 nm in diameter. Due to the limited resolution of our EDX system an elemental analysis is not possible. A comparison of the contrast given by the precipitates in the SEM-micrograph with larger points giving the same contrast suggests that the precipitates consist of Ag and/or Al. Further on, it can be seen in Fig. 2a that the contact spots are directly interconnected with the Ag/Al-finger (green arrow). Partly the interconnection is interrupted by a Pb containing glass layer (red arrow).

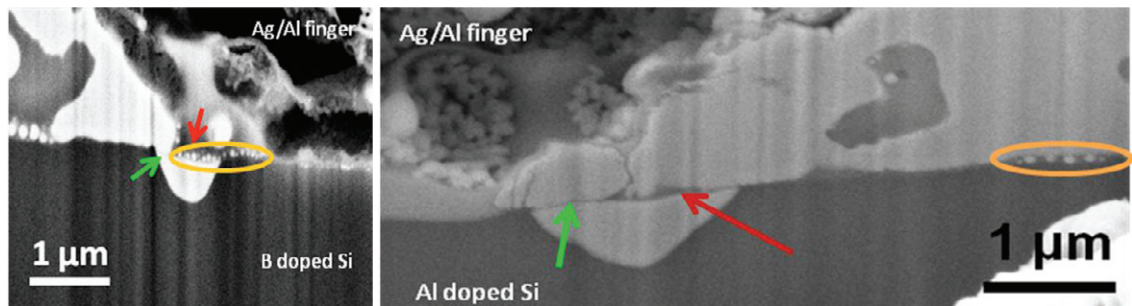


Fig. 2. SEM micrographs of cross sections of Ag/Al thick film paste after etching in $\text{NH}_3:\text{H}_2\text{O}_2$ (1:1). (a) Left: Metallization of B doped p^+ layers with Ag/Al thick film paste. For details see section 3.1; (b) Right: Metallization of Al doped p^+ layers with Ag/Al thick film paste. For details see section 3.2. Orange oval: precipitates at the wafer / Ag/Al-paste interface. Green arrow: contact spots are directly interconnected with the Ag/Al-finger. Red arrow: contact spot - Ag/Al-finger interconnection is interrupted by glass layer.

Low doping (surface doping $\sim 7E15 \text{ cm}^{-3}$)

Contacting p-doped silicon using Ag thick film paste results in contact resistances of 70-170 $\text{m}\Omega\text{cm}^2$. Using Ag/Al thick film paste contact resistances of 1.3-26 $\text{m}\Omega\text{cm}^2$ are obtained. SEM analysis reveals various contact forms as observed for the contact formation to highly p-doped layers (lamellas, silver crystallites, etc.) [2]. Precipitation of Al at the paste/Si interface is observed as well. The formation of Al-rich rectangles around contact spots is not observed. Contact spot size is similar as for the highly B doped substrate: $\sim 0.5\text{-}10 \mu\text{m}$ ($T_{\text{wafer}} = 710^\circ\text{C}$). Table I summarizes the differences in contact formation between differently doped and treated surfaces.

3.2. Doping with aluminum (surface doping $\sim 4E18 \text{ cm}^{-3}$)

No wet chemical treatment of the wafer surface

The surface doping of the samples processed without wet chemical treatment of the wafer surface after removal of the Al-paste is $4E18 \text{ cm}^{-3}$.

Though this is only half the surface acceptor impurity level of the acceptor impurity level of the B doped samples, we find in the SEM interface analysis of samples metalized with Ag thick film paste more Ag crystallites at the contact interface than for B doped surfaces. The Ag crystallites are found all over the metalized surface. Nevertheless, we find more and larger Ag crystallites along the lamellas of the Al-Si eutectic (see Fig. 3). Additionally, the Ag thick film paste etches into the wafer at these structures. Contacting Al doped layers with Ag/Al thick film paste, the SEM interface analysis reveals less substructures within the contact spots than for B doped layers (Al lamellas, Ag pellets, see [2]). Most contact points are filled with an apparently homogenous Ag/Al mixture. Rarely Ag pellets are detected. At the paste/Si interface precipitation of Al is detected (see 3. 3a) as well as Al-rich rectangles around contact points. These rectangles are detected more often than for B doped structures. Additionally, we find a more highly doped area beneath the contacts (thickness: <100 nm up to 650 nm, see Fig. 4a & b). The contact forms not only in the shape of pyramids or ellipsoids but also in "L-form" with varying angles. We observed "L-forms" with angles of approximately 90°, 110-120° and 135° (see Fig. 5). The edges are partly rounded. Contact spot size is ~1-10 μm ($T_{\text{wafer}} = 710^\circ\text{C}$). A difference in number, size or shape of the contact spots for the two peak temperatures applied is not observed ($T_{\text{wafer}} = 625, 710^\circ\text{C}$).

As for the B doped surfaces we detected precipitates at the wafer surface (see Fig. 2b). The precipitates are isolated from the Ag/Al-finger by a Pb containing glass layer. The contact spots are found in direct contact with the Ag/Al finger as well as separated from it by a Pb containing glass layer.

Due to a high amount of finger interruptions the measurement of the specific contact resistance was not possible for the structures printed on Al doped surfaces.

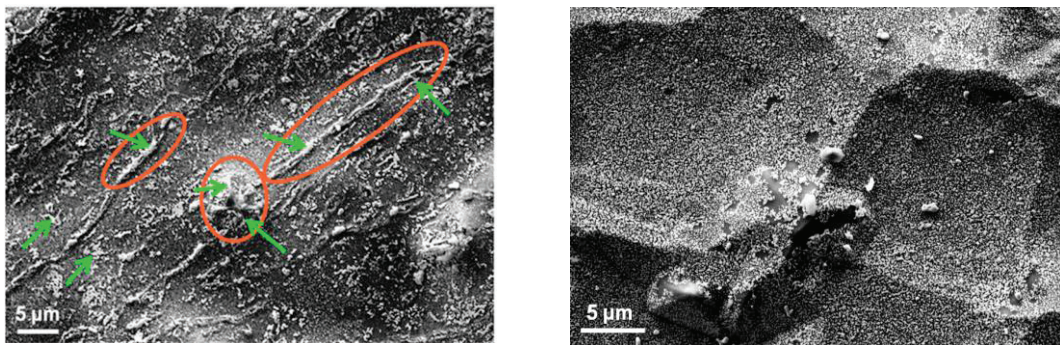


Fig. 3. SEM micrographs of Al doped p^+ layers metalized with Ag thick film paste. Ag thick film paste removed in HF. Ag crystallites are found all over the metalized surface. (a) Left: Wafer surface not wet chemically treated (Al group I): Ag crystallites (e. g. green arrows) are preferably found along the lamellas (red ovals) of the Al-Si eutectic. (b) Right: Wafer surface etched in NaOH_{aq} before metallization (Al group III). Very small Ag crystallites cover the whole wafer surface regardless of the crystal orientation of the surface.

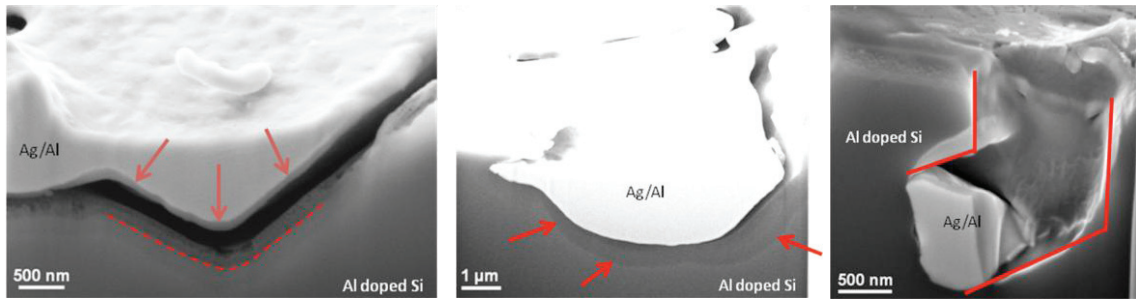


Fig. 4. SEM micrographs of cross sections of Ag/Al contact spots after etching in HF. Metallization of Al doped p^+ layers with Ag/Al thick film paste. (a) Left: Precipitation at the bottom of the contact spot (red arrows) and a higher doped region under the contact (red line).; (b) Middle: Under the contact spot a higher doped region (thickness $\sim 430\text{-}650\text{ nm}$) is visible (red arrows). (c) Right: "L-forms" with angles of approximately 90° , $110\text{-}120^\circ$ and 135° are observed.

Wafer surface chemically polished (HNO_3 , HF, $\text{C}_2\text{H}_4\text{O}_2$)

The surface doping of the samples with chemically polished wafer surface after removal of the Al-paste is $2.3\text{E}18\text{ cm}^{-3}$. The samples contacted with Ag/Al thick film paste reveal contact spots with mainly homogenous filling. The contact forms in the shape of pyramids, ellipsoids and in "L-form" with varying angles (see Fig. 4c). Some Ag pellets are detected. Single Al-lamellas are found. Underneath some of the contact spots we observed a more heavily doped area.

Wafer surface etched in NaOH_{aq} (80°C)

The surface doping of the samples with NaOH -etched wafer surface after removal of the Al-paste is $3\text{E}18\text{ cm}^{-3}$. For the samples metallized with Ag thick film paste we find significantly more Ag crystallites than for the B doped samples and for the Al-doped samples that are not wet chemically treated. On the NaOH_{aq} -etched wafer surface the Ag crystallites cover the whole surface homogeneously. No difference is observed between the $\langle 100 \rangle$ oriented surface and the $\langle 111 \rangle$ oriented surfaces created by etching in NaOH_{aq} . For the samples contacted with Ag/Al thick film paste the contact formation is very similar to the contact formation on the chemically polished samples. Additionally, triangles are found at the $\langle 111 \rangle$ surfaces created by etching in hot NaOH_{aq} (see Fig. 5).

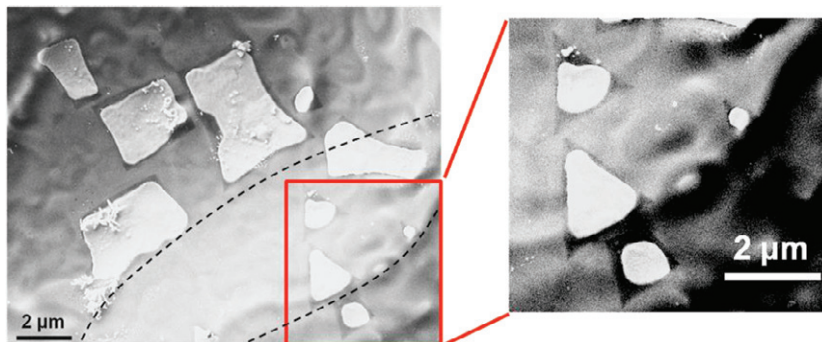


Fig. 5. SEM micrograph of Ag/Al contact spots after etching in HF (top view). Al doped p^+ layers, surface etched in hot NaOH_{aq} before metallization with Ag/Al thick film paste. Black lines mark a $\langle 111 \rangle$ oriented surface area caused by etching in hot NaOH_{aq} .

Table 1. Comparison of contact structures for Al and B doped surfaces.

	Dopant Acceptor impurity level @ surface	B 7E15 cm ⁻³	B 9E18 cm ⁻³	Al 4E18 cm ⁻³	Al 2.3E18 cm ⁻³ CP	Al 2.3E18 cm ⁻³ NaOH
Ag- paste	Ag crystallites Size of the crystallites	Very few <200 nm	Very few <200 nm	Some up to 700 nm	No sample	Many <400 nm
	Shape and size of the contact spots	Pyramidal, ellipsoid, 1-10 μm	Pyramidal, ellipsoid, 1-10 μm	Pyramidal, ellipsoid, L- shaped, 1-10 μm	Pyramidal, ellipsoid, L- shaped, 1-10 μm	Pyramidal, ellipsoid, L- shaped, 1-10 μm
	Filling	Many substructures	Many substructures	Homogenous	Some substructures	Some substructures
Ag/Al- paste	Al lamellas	Often	Often	Very few	Some	Some
	Ag pellets	Often	Often	Some	Some	Some
	Al rectangles around contact points	Not observed	Often	Very often	Very often	Very often
	Precipitation of Al @ paste-Si interface	Not observed	Often	Very often	Often	Often
	Higher doped layer under contact point	Not observed	Not observed	Observed	Observed	Observed

4. Discussion

The main differences in the contact formed by Ag/Al thick film paste to p⁺ Si surfaces doped with B and Al, respectively, are the formation of a higher doped area underneath the contact spots, the formation of “L-formed” contact spots and the more homogenous filling of the contact spots for Al doped surfaces.

The formation of a higher doped area underneath the contact spots is only observed for contact formation with Ag/Al thick film paste to Al-doped substrates. Contacting B-doped substrates with Ag/Al thick film paste we do not observe a more heavily doped area underneath the contact spots. This is not expected, as we observed the formation of Al-rich rectangles around the contact spots for B doped substrates as well as for Al-doped substrates. Therefore, the question arises, if the Ag/Al contact spots attract Al from the Al-doped surface.

The formation of contact spots in “L-shape” can be explained by the fact, that Al prefers <111> surfaces for contact formation, as we observed before [6].

The surface structure influences the contact formation to Al doped Si with Ag/Al thick film paste as well as with Al thick film paste. For Ag/Al thick film paste the filling of the contact spots is more homogenous for rougher surfaces (no wet chemical treatment) than for smoother ones (chemically polished, etched in NaOH_{aq}). For contact formation with Ag thick film paste the size of the Ag crystallites increases for increasing surface roughness. Interestingly, we observe more Ag crystallites on the NaOH_{aq} etched surface than on the rougher chemically untreated surface.

In case of n⁺-Si it is commonly assumed that the growth of Ag crystallites is enhanced by crystal defects induced by P doping [4, 7, 8]. B is said to introduce more defects into the wafer than P, especially in case of BBr₃ and POCl₃ diffusion. Therefore, more Ag crystallites should be detected on B than on P emitters. But it is well known that only few crystallites are formed on B emitters when contacted with Ag thick film paste (e.g. [1-3]). The Al doped layers are formed by recrystallization of the Al-Si melt [9]. Nevertheless, solar cells with high efficiencies and V_{oc} are processed with Al doped emitters (e.g. [10]). Therefore, we assume less damage induced by the recrystallization of the Al-Si melt than by diffusion of B, but more than induced by P. With this assumption we can explain the higher amount of Ag crystallites

on Al doped emitters than on P-doped emitters. The reason for the reduced Ag crystal growth on B doped surfaces must be different.

For contacting p⁺-Si with Ag/Al thick film paste the contact spots are partly in direct contact with the Ag/Al finger and sometimes isolated by a Pb containing glass layer. This implies the current transport takes place via contact spots in direct contact with the Ag/Al finger and via a tunneling mechanism through the thin glass layer, as proposed for the n⁺-Si/Ag thick film contact [4].

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References

- [1] Lago R, Pérez L, Kerp H, Freire I, Hoces I, Azkona N. Screen printing metallization of boron emitters. *Prog Photovolt Res Appl* 2010;**18**:20-7.
- [2] 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/WCPEC-5, Valencia* 2010; 2353-6.
- [3] Kerp H, Kim S, Lago R, Recart F, Freire I, Pérez L et al. Development of screen printable contacts for p⁺ emitters in bifacial solar cells. *Proc. 21st EU PVSEC, Dresden* 2006; 892-4.
- [4] Schubert G, *Thick film metallization of crystalline silicon solar cells: mechanisms, models and applications*. PhD thesis, University of Konstanz, 2006.
- [5] R. Kopecek, T. Buck, J. Libal, R. Petres, I. Röver, K. Wambach et al. Large area n-type multicrystalline silicon solar cells with B-emitter: efficiencies exceeding 14%. *Proc. 15th IPSEC, Shanghai* 2005.
- [6] Riegel S, Terheiden B, Hahn G. On the metallization of boron back surface fields, *2nd Workshop on Metallization, Konstanz, Germany* 2010.
- [7] Pysch D, Mette A, Filipovic A, Glunz SW. Comprehensive analysis of advanced solar cell contacts consisting of fine-line seed layers thickened by silver plating. *Progr Photovolt Res Appl* 2009;**17**:101-14.
- [8] Mette A. *New concepts for front side metallization of industrial silicon solar cells*. PhD thesis, Albert-Ludwigs-Universität Freiburg, 2007.
- [9] Huster F. Investigation of the alloying process of screen printed aluminium pastes for the BSF formation on silicon solar cells. *Proc. 20th EU PVSEC, Barcelona* 2005; 1446-9.
- [10] Schmiga C, Hörteis M, Rauer M, Meyer K, Lossen J, Krokoszinski HJ et al. Large-area n-type silicon solar cells with printed contacts and aluminium-alloyed rear emitter. *Proc. 24th EU PVSEC, Hamburg* 2009; 1167-70.