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Investigation of Contact Resistivity on a Laser Doped Boron Emitter from CVD Doping Layers

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Abstract. In this study, the contact formation to a p^+-doped emitter created by laser irradiation is investigated. We examine the influence of different firing temperatures and paste compositions on the contact formation on Si substrates after laser treatment of the Si surface. Commercially available AgAl and Ag pastes are screen-printed on the Si wafers. The formed contacts show low contact resistivity ≤ 2 mΩcm^2 for both pastes within the investigated firing temperature ranges. Furthermore, top view investigations of the formed contacts by electron scanning microscopy revealed: for the AgAl containing paste typical AgAl spikes grow into the Si surface; for the Al-free Ag paste small Ag crystallites grow. In addition, a new structure is observed on the contact surface. Using energy dispersive X-ray spectroscopy, Ag as an incorporated part of this structure has been identified. This structure can be considered as an AgSi alloy, covering most of the contact surface. This potentially explains the low contact resistivity values in case of the Ag paste.

INTRODUCTION

In the past years n-type silicon base material has become a factor of growing importance. This is due to the advantages provided by this material. It has a high tolerance for many metal impurities and shows no light-induced degradation (LID). With this the contacting of p^+-doped emitters has also become important. There were different experiments focusing on the contact formation on these emitters. Past experiments showed that pure Ag pastes led to rather high contact resistivity, but by adding a small amount of Al to the Ag paste the contact resistance could be lowered, as shown by Kopecek et al. [1]. Kerp et al. [2] verified these results and investigated the influence of the Al content in the paste. High Al content led towards lower contact resistivity but also increased the risk of shunting. Investigations of the contact surface showed large AgAl spikes, growing into the silicon surface. These spikes were the reason for the risk of shunting the p-n junction. By growing deep into the surface they can penetrate the emitter and provide an alternative path for the generated current. This leads to lower V_{OC} and lower efficiency of the solar cell. The formation of these spikes was investigated by Fritz et al. [3], [4]. Since AgAl paste shows the risk of shunting, the use of pure Ag paste for contacting is desirable. Engelhardt et al. [5] showed that low contact resistivity with pure Ag paste is also possible. For this reason both an AgAl and a pure Ag paste are investigated in this contribution.

All these previous experiments focused on textured surfaces, but in case of a laser doped surface the topography changes significantly. The first who created a p-n junction with a laser were Fairfield and Schwuttke [6]. The actual advantage of laser doping is that the laser doping process works locally, i. e. no additional masking step is necessary. This enables the creation of highly doped areas underneath the contact fingers by laser irradiation and a lowly doped emitter area in between. This selective emitter approach aims at a higher blue response of the solar cell and lower contact resistivity values. The contacting of laser doped surfaces was investigated by Fernandez-Robledo et al. [7]. They showed that a laser melted highly doped surface led to low contact resistivity (~5 mΩcm²). Since the laser doping process works locally, no additionally masking step is necessary. The laser melts the silicon surface locally and allows a fast diffusion of the dopant atoms. Afterwards the surface recrystallizes epitaxially leading to highly doped areas where the Si surface was molten. This epitaxially recrystallized surface shows a distinct difference to the textured surface. Contact formation on this recrystallized surface has not yet been intensively studied.

In this work we present an investigation of the contact resistance of Ag and AgAl pastes screen printed on n-type Si wafers, after laser based diffusion of a highly doped boron emitter. We produced samples exclusively for transfer length measurements (TLM) with laser doped full area emitter regions to investigate the contact resistance on laser melted and recrystallized surfaces. Afterwards the metal contacts on selected samples were stripped in hydrofluoric acid. The surface of these samples was then investigated using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX).

EXPERIMENT

We used n-type Cz-Si (Czochralski) samples (156 mm x 156 mm, pseudo square) with a base resistivity of 4.5 Ωcm. These samples received a wet chemical alkaline surface texture followed by a boron silicate glass (BSG) deposition using plasma-enhanced chemical vapor deposition (PECVD). Using the BSG layer as doping source, laser doping was used without any prior diffusion to achieve full area doping without a lowly doped area between the contact fingers. We used a ns-laser with a wavelength of 532 nm. Afterwards the BSG was removed by hydrofluoric acid and a layer of thermal SiO_x (~7 nm) at 900°C was grown as passivation layer. This was the only high temperature step in the process. A PECVD SiN_x deposition followed. The different areas for the TLM structures were then isolated by laser cutting to prevent lateral current flow among each other. The metal contacts were screen-printed on the highly doped areas and fired in a standard belt furnace at a set peak firing temperature range from 770°C to 870°C. The contact resistivity was measured using the TLM method. The effect of temperature variation on the contact formation was investigated by SEM and EDX for lowest and highest peak firing temperature. For these studies, the contact fingers and passivation layers were removed by using aqueous 5% HF solution.

RESULTS AND DISCUSSION

We used a fluence of 2.5 J/cm² for laser doping and thereby created a 70 Ω/□ emitter. The surface concentration of the boron emitter is $1.2*10^{19}$ cm^{-3} with an overall doping depth of approximately 700 nm. This was determined by electrochemical capacitance voltage measurement (ECV); the dopant profile is displayed in Fig 1. The sample received no high temperature treatment; the doping profile is the result of laser treatment only. The depth of the boron diffusion depends on the melting depth of the laser process. This leads to a kink in the concentration profile and an abrupt decrease at around 0.7 µm. The blue part at the end of the curve shows the base doping.

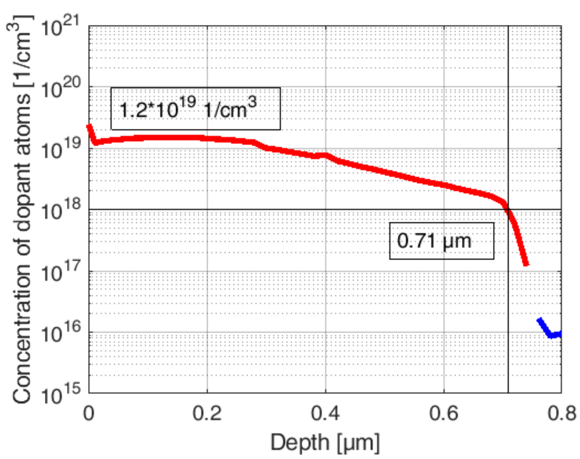

FIGURE 1. ECV measurement of the boron emitter structure. The surface concentration is $1.2*10^{19}$ cm^{-3}. The profile shows a clear kink at 0.7 µm and the concentration drops rapidly to the base doping.

The results of our contact resistivity study varying the paste and peak firing temperature are shown in Fig. 2 for the lowest T1 (770°C) and the highest peak firing temperature T2 (870°C). All parameter combinations of peak firing temperature and metal paste show low resistivity values with mean contact resistivity below 2 mΩcm². No significant trend for the different peak firing temperatures is found, as the results in contact resistivity for all samples are evenly distributed for all investigated temperatures. This shows the wide firing window for solar cells with laser doped emitter structures for commercially available pastes. To get a more detailed understanding of the formed contacts, we use SEM to investigate the surface after removing both the passivating glass layer and the metal fingers.

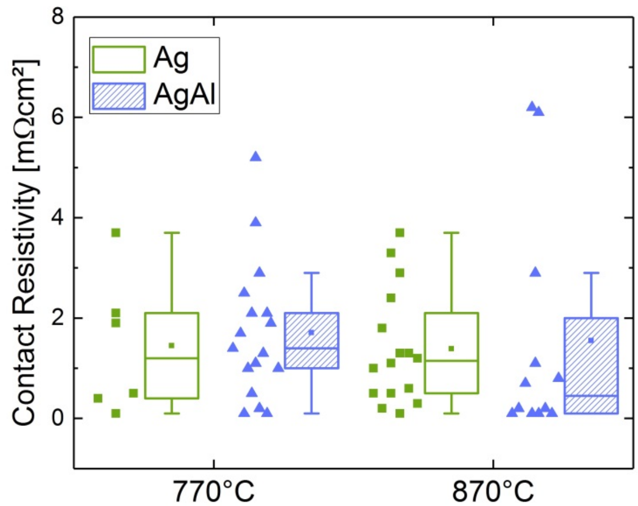

FIGURE 2. Measured contact resistivity of the processed TLM structures for the lowest and highest peak firing temperature. Results for the Ag paste are shown by the empty boxes, AgAl paste results are shown by the shaded boxes.

In Fig. 3 the contacted area for samples screen-printed with AgAl paste and etched in 5% HF acid is shown. (left: fired at T1, right: fired at T2). The upper part deals with the topography, the lower part with the material contrast. The laser process generated a rather flat topography despite the former texture. The surface is corroded due to the glass frit etching. The rectangle-like features in different sizes, marked with red circles on the left side for both samples, are inverted AgAl pyramids grown deep into the silicon surface. At firing temperature T1 these spikes are only 1-2 µm wide and appear alone or in small groups. These spikes appear rarely on the surface. At higher firing temperature T2 the spikes are up to 3-5 µm wide. Groups of spikes on this sample are formed by a higher number of spikes and the distance between the groups is smaller compared to those of samples fired at T1. Experiments on textured wafers demonstrate similar results [4]. These spikes are able to penetrate the emitter, leading to shunting of the p-n-junction and increased saturation current J_{0E} [8]. Higher peak firing temperatures result in deeper spikes. Therefore, reaching low contact resistivity with lower peak firing temperatures is desirable.

The surface view of samples contacted with Ag paste is shown in Fig. 4 (T1 left, T2 right side). On the upper half of Fig. 4 the topographies, on the lower side the material contrasts are shown. For T1 individual Ag crystals are distributed on the surface and additionally a continuous layer is covering the wafer surface. In the topographic view the surface shows brighter, slightly rougher areas. In the material contrast some of these structures show a high material contrast compared to silicon. This surface layer could be responsible for the low contact resistivity even for low peak firing temperatures. Due to the higher number of Ag crystallites grown on the sample fired at T2, it is difficult to decide whether the same continuous layer can be found on this surface.

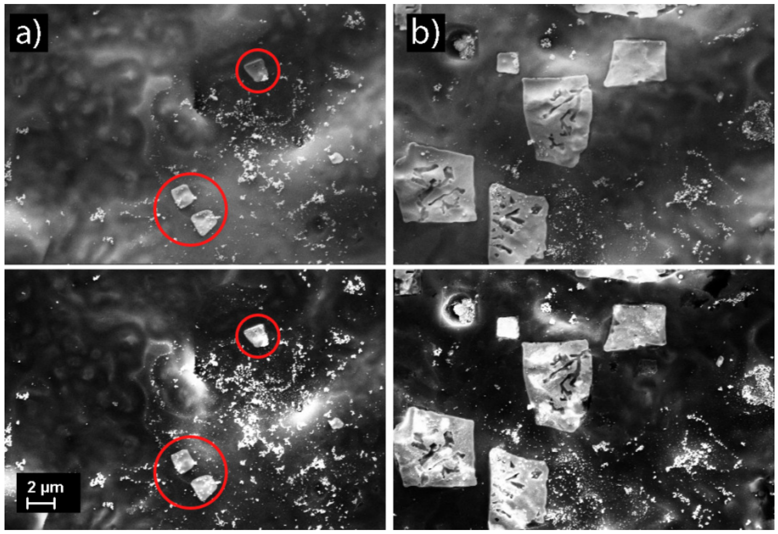

FIGURE 3. SEM top view on a laser treated highly doped surface contacted with AgAl paste after contact etching in 5% HF acid. The upper part shows the topography, the lower part the material contrast. The wafer on the left part of the image (a) was fired at a low peak firing temperature T1; the one on the right part of the image (b) was fired using a high peak firing temperature T2.

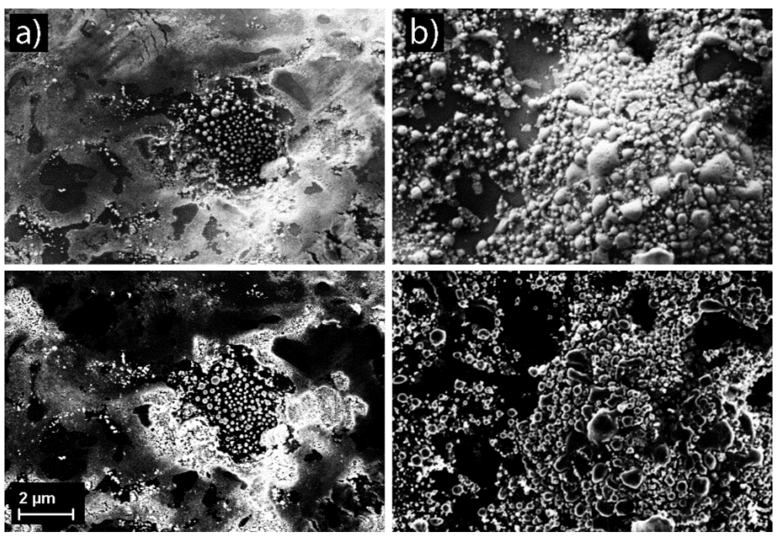

FIGURE 4. SEM top view on a laser treated highly doped surface contacted with Ag paste after contact etching in 5% HF acid. The upper part shows the topography, the lower part the material contrast of the same area on the samples for (a) and (b). The sample shown in the SEM image on the left side (a) was fired at a low peak firing temperature T1, the sample shown in the SEM image in the right (b) was fired using a high peak firing temperature T2.

The structure contains Ag, as deduced from EDX measurements displayed in Fig. 5. This structure could possibly be an AgSi alloy with a composition of Ag with 0.93 atomic percent Si at the eutectic temperature [9]. This alloy could be formed due to laser defects on the surface. As shown by Hameiri et al. [10], the number of defects on the surface grows depending on the recrystallization velocity after laser melting. It could be possible that the alloy is formed near these defects due to a eutectic reaction of Ag and Si. Si is able to diffuse inside Ag at temperatures well below the eutectic temperature of 830°C [11]. For the Ag in the vicinity of defects the process could lead to the growth of this alloy even for temperatures below the melting temperature.

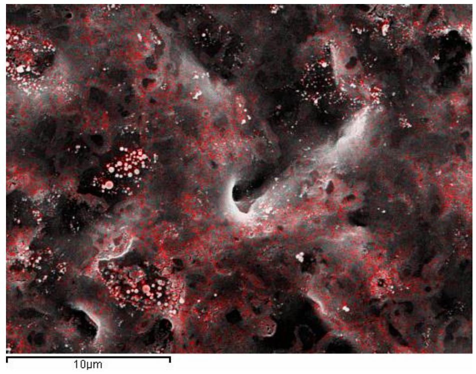

FIGURE 5. EDX measurement of a sample contacted with pure Ag paste and fired at T1 peak firing temperature. The red dots show measured Ag on the sample, showing that Ag is distributed all over the wafer surface.

CONCLUSION

Contacts with low contact resistivity on laser doped boron emitters from PECVD doping layers were demonstrated. For both AgAl and pure Ag paste low contact resistivities below 2 mΩcm² could be achieved for a wide range of peak firing temperatures. SEM images of the etched-back contact surfaces revealed AgAl spikes that are already known from textured samples. These spikes had a width of about 1-2 µm and appeared only rarely on the wafer surface for low peak firing temperatures. A high peak firing temperature led to larger spikes of 3-5 µm width in larger groups, both in size and number, that where more frequent. The pure Ag paste showed small Ag crystals on the surface, with growing numbers for higher temperatures. Additionally, a new layer covering the contact surface was detected. EDX revealed Ag being part of this structure. This structure could be an AgSi alloy.

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