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Microstructural and electrical properties of different-sized aluminum-alloyed contacts and their layer system on silicon surfaces

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ABSTRACT

The firing of screen-printed aluminum pastes is well established for the formation of a back surface field (BSF) and back contacts since many years in silicon solar cell fabrication. In this paper we investigate the electrical and microstructural properties of Al-alloyed contacts and their layer system, consisting of (i) the Al-doped p^+-layer (2–14 μm), the eutectic layer (1–15 μm) and the layer of paste residuals (20–100 μm). We show the influence of process parameters like the amount of printed paste, the alloying time and the peak temperature. Special emphasis is devoted to the properties of small alloyed screen-printed aluminum structures for the formation of local aluminum back contacts. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), electrochemical capacitance voltage (ECV) and conductivity measurements have been applied to characterize the samples. A simple model is qualitatively augmented to describe all effects occurring in a technical alloying process. For example, for increasing aluminum amounts, a saturation of the p^+-layer thickness was found in the range of 10 mg/cm^2. For small screen-printed structures, the p^+-layer is formed very homogenously and with a greater thickness compared to samples with a full-area Al metallization, which have been processed with similar alloying conditions. For the eutectic layer a high electrical conductivity of about 16×10^6 S/m, only 2–3 times below that of pure aluminum has been determined. This is advantageous for the lateral conductivity especially for high paste amounts and small structures, which feature a relatively thick eutectic layer.

1. Introduction

The formation of aluminum-alloyed p^+-layers (Al-p^+-layers) by screen-printing and firing of Al pastes has already been used for many years in industrial p-type solar cell production lines to realize a full-area back surface field (BSF) and the back contact. Cell concepts as the n^+np^+ cell [1,2] use the cost-saving process of Al-alloying for the fabrication of back-junction solar cells with a full-area Al-p^+ rear emitter. A further promising approach is the realization of back-contact back-junction cells (BC–BJ) on n-type material with Al-p^+-layers as local rear emitters [3–5]. By full-area screen-printing of Al paste on a masking dielectric layer in an i-PERC cell [6] (industrially passivated emitter and rear) the influence of the relatively high saturation current density J_{0e} of the Al-p^+-layer [7,8] can be reduced by limiting its area. Another approach to reduce the J_{0e} is the application of a passivation layer on the Al-doped Si surface [9,10].

For local Al-p^+-layers processed by full-area screen-printing of Al on locally opened dielectric layers, a penetration depth of up to 60 μm in the alloyed areas has been reported [11,12]. This has been explained by the large amount of aluminum next to the opened areas. This means that no saturation of aluminum with silicon is reached during alloying, resulting in a large driving force to dissolve silicon from the surface.

This work deals with another method for the formation of local p^+-layers by screen-printing and firing of small Al structures. This alternative is quite different in comparison to the above mentioned one as there is only a limited Al amount available. Also on samples with a full-area Al metallization the locally available amount of Al is limited, so similar results are expected. Using this process of alloying small Al structures to form local Al emitters for a BC–BJ cell, high efficiencies of up to 19.7% have been achieved [5].

In this paper detailed investigations of microstructural and electrical properties of different-sized aluminum-alloyed contacts and their layer system on silicon surfaces are presented. Cross-sections of the samples have been prepared by ion-beam-polishing. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) have been applied to analyze

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the microstructures of the three layers: (i) Al-p^+-layer (2–14 μm), (ii) eutectic layer (1–15 μm) and layer of paste residuals (20–100 μm). Furthermore, the electrical properties are investigated with sheet-resistance and electrochemical capacitance voltage (ECV) measurements.

2. Alloying of aluminum on silicon surfaces

After screen-printing of Al paste on a Si surface the Al-p^+-layer is formed during a short firing step of few seconds. The alloying process can be explained using the Al–Si binary phase diagram [13] (see Fig. 1) and is illustrated in Fig. 2.

(a) The firing process starts with the burning out of organic solvents from the paste.

(b) The aluminum oxide shells of the particles are thickened due to high temperatures and an oxygen containing atmosphere. The particle matrix is therefore stabilized and not destroyed during the firing process [13,14]. At 660 °C aluminum melts and dissolves silicon from the surface to form a liquid Al-Si-phase with a temperature dependent percentage of silicon according to the liquidus curve $L(T)$ of the phase diagram.

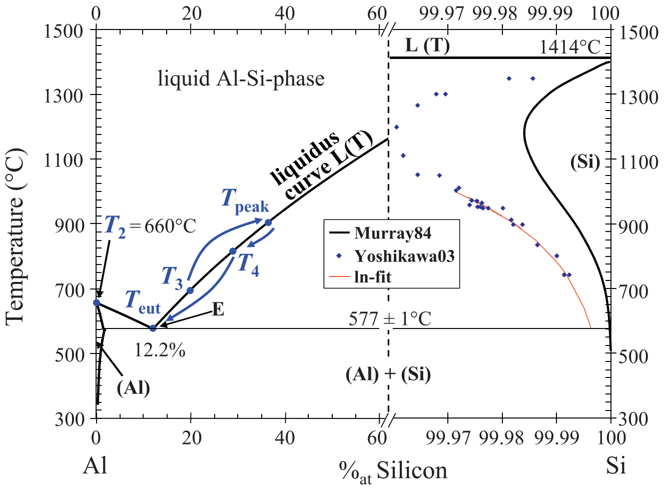

Fig. 1. Al–Si binary phase diagram after [17] silicon rich sector at the right (including solid solubility data from [18] and empirical fit used for calculations). The indices of temperatures correspond to Fig. 2. E-eutectic; point (Al) or (Si)-silicon or aluminum in solid phase.

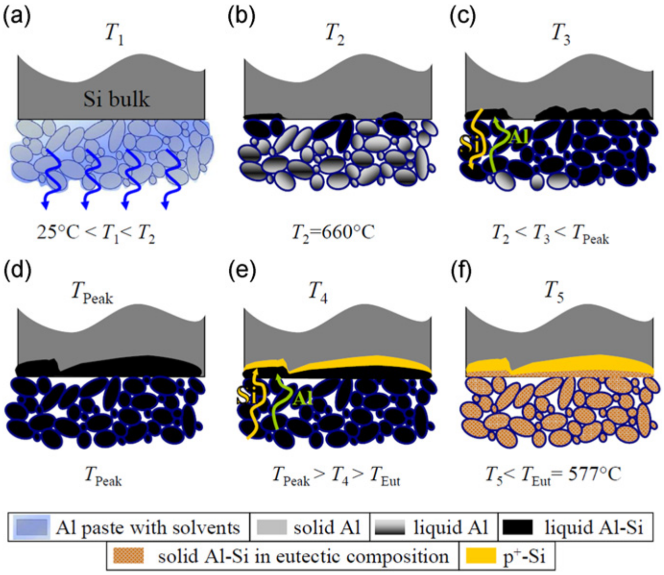

Fig. 2. Schematic illustration of the alloying process after [13], explanations in the text.

(c) Si diffuses via small interconnections into the particles and Al diffuses to the wafer surface where a “lake” of liquid Al–Si phase is built. The silicon content in the liquid phase on the wafer surface and in the particles increases at higher temperatures.

(d) At peak temperature, the maximum concentration of silicon in the liquid phase and so the maximum amount of dissolved silicon is reached. Therefore the weight of dissolved silicon $m_{\mathrm{Si,dis}}$ and the corresponding thickness $d_{\mathrm{Si,dis}}$ can be calculated with the weight of deposited aluminum m_{Al} according to [15]:

$$d_{\mathrm{Si,dis}} = \frac{m_{\mathrm{Si,dis}}}{A\rho_{\mathrm{Si}}} = \frac{m_{\mathrm{Al}}}{A\rho_{\mathrm{Si}}} \times \frac{L(T_{\mathrm{peak}})}{100-L(T_{\mathrm{peak}})} \qquad (1)$$

where A is the (homogeneously) printed area, ρ_{Si} the density of silicon and $L(T_{\mathrm{peak}})$ the percentage of Si in the liquid Al-Si-phase at peak temperature T_{peak}.

(e) While cooling down, Si is rejected from the liquid phase and crystallizes at the liquid-phase/silicon interface. According to the solid solubility (Fig. 1, right), which decreases with falling temperature in the relevant temperature range, Al atoms are incorporated into the Si lattice. This means that the peak doping concentration is situated at the former liquid-phase/silicon interface with decreasing doping concentrations in direction to the final surface of the p^+-layer.

(f) When the eutectic temperature of $T_{\mathrm{eut}} = 577$ °C is reached, the remaining liquid phase solidifies in a short time. The silicon percentage of this mixture is still relevant (theoretical eutectic composition with 12.6 Wt% Si). Between the surface of the p^+-layer and the paste matrix remains therefore the so called “eutectic layer” with a compact structure consisting of nearly pure aluminum and about 12.6 Wt% silicon in the typical lamella structure [16] of eutectic alloys. The porous layer of paste particles at the outer surface (paste residuals) consists of a solid Al–Si mixture as well.

In Fig. 3 a scanning electron microscope (SEM) picture with the resulting layer composition is shown. Due to the potential contrast [19], the interface between Al-p^+-layer and Si bulk is visible in the SEM and can be used for homogeneity analyses and thickness measurements.

As the particles were stabilized by the oxide shells, the volume of the paste particles after alloying can be assumed to be the same as before and also the amount of aluminum (percentage of aluminum in the p^+-layer is negligible). The volume of the eutectic layer therefore corresponds to the proportion of silicon in the eutectic layer and the paste particles and the thickness of the eutectic layer d_{eut} can be calculated with $L(T_{\mathrm{eut}})$, the Si-percentage in the liquid phase at eutectic temperature,

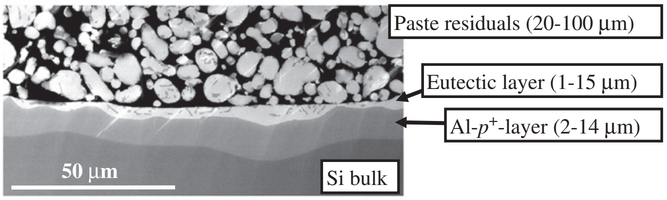

Fig. 3. SEM image of a cross-section of an alloyed Al contact prepared by ion-beam-polishing with typical thicknesses of the different layers.