



Quantitative theoretical and experimental analysis of alloying from screen-printed aluminum pastes on silicon surfaces



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ABSTRACT

In this study, we present detailed theoretical and experimental investigations on full-area alloying from screen-printed aluminum pastes on silicon surfaces for solar cell applications. We introduce a simple analytical model for the description of the alloying process derived from existing models for evaporated Al layers, which we adapt to printed Al pastes. Thereby, we particularly account for the recrystallization of Si within the paste particles, which we refer to as parasitic Si recrystallization. Applying our model, we demonstrate good accordance of calculated with measured eutectic layer thicknesses. We show that the model can be versatily used to investigate screen-printed Al-alloyed contacts in detail: We demonstrate that the latent heat of the Al paste significantly influences the alloying process. Thus, the effective peak temperature of the alloying process can be several 100 °C below the set peak temperature of the firing furnace. By combining calculations of the effective peak temperature with measurements of the Al doping concentration, we determine a parameterization of the solid solubility of Al in Si down to the eutectic temperature of 577 °C. Our investigations therefore provide improved understanding of alloying from printed Al pastes and enable the specific optimization of Al-alloyed contacts.

1. Introduction

Since alloying from screen-printed aluminum pastes has been established in the fabrication of silicon solar cells [1] and led to the introduction of the so-called aluminum back surface field (Al-BSF) solar cell, many studies have dealt with investigating the alloying process [2–8] and the structural and electrical properties of the Al-doped p^+ Si (Al- p^+) regions forming in the full-area metal contacts [9–15] for solar cell applications. Thus, the steps of the alloying process are well-known and schematically shown in Fig. 1. During alloying, Al melts within the paste particles and Si dissolves into the melt from the Si wafer surface. As Al atoms are thereby displaced from the paste particle shells, the liquid Al-Si phase expands to the wafer surface, where a lake of melt forms. The dissolution of Si proceeds up to the peak temperature in a typical range of 800–900 °C, at which the maximal amount of Si is present within the melt. During cooling down afterwards, Si is rejected from the melt to recrystallize epitaxially at the wafer surface. Thereby, Al atoms are incorporated into the Si lattice, forming the Al- p^+ region with typical thicknesses of 4–8 μm. At the eutectic temperature of 577 °C, the remaining melt instantly solidifies to form (i) a compact layer of eutectic composition with a Si percentage of 12.6 wt% [21] on top of the Al- p^+ region and (ii) the Al-Si eutectic within the paste particle shells.

For describing the alloying process from evaporated Al layers on Si quantitatively, there are analytical models available in the literature [15]. For printed Al pastes, which exhibit an entirely different structure [3,8,16,17], these models need to be adapted. Additional effects, originating from the shape and size distribution of the particles of the Al paste, need to be taken into account. It has been reported that Si recrystallization does not only occur at the Si wafer surface, but also takes place within the paste particles [3,8] as the particle shells represent effective Si seed crystals [18,19]. Thus, the existing analytical models can significantly overrate the thickness of the Al- p^+ region at the Si surface, which determines the recombination characteristics of the Al contact by shielding electrons from the recombination-active surface [8,9,12,15]. We therefore denote the Si growth in the paste particles as *parasitic Si recrystallization*. Neglecting this effect can lead to a miscalculation of the electrical properties.

In this study, we therefore derive a quantitative model for the description of alloying from screen-printed Al pastes, which takes parasitic Si recrystallization into account. We investigate the difference of set and effective peak temperature of the alloying process and determine the solid solubility of Al in crystalline Si as two applications of our model.

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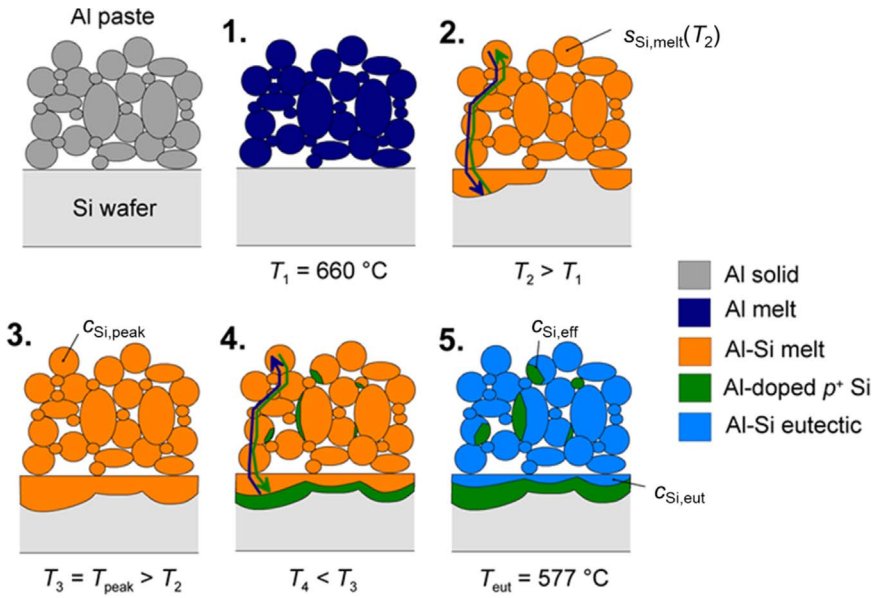


Fig. 1. Qualitative model for the alloying from screen-printed Al pastes (graph adapted from [3]). After reaching the melting temperature of Al, the Al melts within the paste particles (1) and Si dissolves from the surface into the melt, adopting the concentration $s_{\text{Si,melt}}$ (2). At the peak temperature, the Si concentration $c_{\text{Si,peak}}$ is maximal (3). While cooling down, Si is rejected from the melt to recrystallize epitaxially at the Si wafer surface or within the paste particles (4). At the eutectic temperature T_{eut} , the remaining melt solidifies to form the eutectic layer exhibiting a Si concentration $c_{\text{Si,eut}}$. Due to parasitic Si recrystallization, the Si concentration $c_{\text{Si,eff}}$ within the paste particles can be significantly higher than $c_{\text{Si,eut}}$ (5).

2. Experimental

We have fabricated a set of simple test samples featuring a comprehensive variation of Al-alloyed contacts using shiny-etched (100)-oriented float-zone silicon wafers with a diameter of 100 mm. The samples were chemically cleaned and a non-fritted Al paste without boron additives was printed onto one surface of the wafers, thereby applying paste amounts of 8.1, 16.6 and 25.6 mg/cm² (measured before drying). Then, the samples were dried to remove the solvents and the Al contacts were alloyed during a short firing step in a conveyor belt furnace at a set peak temperature $T_{\text{peak,set}}$ of 900 °C for different peak temperature times $t_{\text{peak,set}}$ from 3.5 to 8.2 s, thereby placing the samples on dummy wafers for cleanliness. Part of the samples was subsequently etched in hydrochloric acid (HCl) to remove the paste residues and the eutectic layers.

For characterization, the thicknesses of the eutectic layers d_{eut} and the Al- p^+ regions $d_{\text{Al-p}^+}$ were measured on ion-polished sample cross sections by means of scanning electron microscopy (SEM). We have carried out electrochemical capacitance-voltage (ECV) measurements to determine the Al acceptor profiles. The profiles have thereby been corrected for the roughnesses of the p^+ region surfaces, which were determined by means of confocal microscopy. In addition, as proposed by Huster [3], the samples were weighed at different stages of the fabrication process: (i) before and (ii) after printing of the paste, (iii) after firing and (iv) after HCl etching.

3. Derivation of a model for alloying from screen-printed Al pastes

In this section, we derive a simple quantitative model for alloying from screen-printed Al pastes by extending the existing model for alloying from evaporated Al layers [15] by characteristic features of printed pastes [3,8,10]. In particular, we account for parasitic recrystallization of Si within the paste particles.

For the analytical calculation, thermal equilibrium conditions are assumed, which particularly implies that the alloying process is completely described by the binary Al-Si phase diagram [21]. For convenience, we thereby separate the alloying process into (i) the dissolution of Si from the wafer surface during heating-up and (ii) the recrystallization of Si during the subsequent cooling. For further details, please see [22].

3.1. Dissolution of silicon

Initially, the paste consisting of aluminum particles of mass $m_{\text{Al},0}$, solvents and organic binders is screen-printed onto the silicon wafer surface. The Al particles exhibit a volume of $V_{\text{Al}}^{\text{part}} = m_{\text{Al},0} / \rho_{\text{Al}}$, with ρ_{Al} standing for the Al mass density. After the solvents have been removed by drying, the Al contact is alloyed during a short firing process, following the five steps displayed in Fig. 1.

(1, 2) After reaching the Al melting point of 660 °C [20], Al liquidizes within the paste particle shells and Si dissolves into the Al melt from the Si wafer surface according to the liquid solubility $s_{\text{Si,melt}}$ of Si in the melt. Since, to the authors' knowledge, there is no parameterization for $s_{\text{Si,melt}}$ available in the literature, we have fitted an Arrhenius relation to the data of reference [21]:

$$s_{\text{Si,melt}}(T) = 685.08 \cdot \exp\left(-\frac{0.294 \text{ eV}}{k_B(T - T_{\text{az}})}\right) \text{ at\%}, \quad (1)$$

with the temperature T given in degrees Celsius, k_B standing for the Boltzmann constant and $T_{\text{az}} = -273.15$ °C for the temperature of absolute zero. Due to thermal equilibrium conditions, Si is distributed homogeneously within the Al-Si melt, such that $s_{\text{Si,melt}}$ is spatially independent. Note that for the following equations, $s_{\text{Si,melt}}$ has to be converted from at% to wt%.

In the following, we derive an analytical expression for the mass of Si dissolved from the surface.

Because the particle shells, which are composed of aluminum oxide, remain stable during the entire alloying process [3], the volume of the paste particles remains constant. Therefore, the Al and Si masses $m_{\text{Al}}^{\text{part}}$ and $m_{\text{Si}}^{\text{part}}$ of Al and Si of the melt within the paste particles at the temperature T_2 can be calculated:

$$\frac{m_{\text{Al},0}}{\rho_{\text{Al}}} = \frac{m_{\text{Al}}^{\text{part}}(T_2)}{\rho_{\text{Al}}} + \frac{m_{\text{Si}}^{\text{part}}(T_2)}{\rho_{\text{Si}}} = \frac{1 - s_{\text{Si,melt}}(T_2)}{\rho_{\text{Al}}} \cdot m_{\text{AlSi}}^{\text{part}}(T_2) + \frac{s_{\text{Si,melt}}(T_2)}{\rho_{\text{Si}}} \cdot m_{\text{AlSi}}^{\text{part}}(T_2), \quad (2)$$

with ρ_{Si} standing for the Si mass density, $m_{\text{AlSi}}^{\text{part}}$ for the mass of the entire Al-Si melt within the paste particles and $s_{\text{Si,melt}}$ given in wt%. Please note that, for convenience, our model does not account for the phase and temperature dependency of the Al and Si mass densities [18,23].

By rewriting Eq. (2), the mass of the Al-Si melt within the paste particles is given by

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