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Study on the front contact mechanism of screen-printed multi-crystalline silicon solar cells

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ABSTRACT

The two key issues of front contact of screen-printed multi-crystalline silicon have been studied. Firstly, the effects of doping profiles in the emitter on the contact-resistance have been systematically investigated. Constant source diffusion is used to explain the doped phosphorus profile in the textured emitter by simulation. Secondly, the penetration mechanism of silver into SiN_x layer was studied by using SEM and EDX to reveal the microstructure of the Ag/Si contact. A model has been proposed to explain the formation of the ohmic contact. It is found that the effectiveness of the contact is determined by the direct contact area of the silver crystallites to both the emitter and the finger. For a commercial multi-crystalline silicon solar cell of 156×156 mm^2, the optimal contact-resistance of about 1.2 mΩ is suggested, corresponding to the doping sheet resistance of around 80–90 $\Omega/\square$. Multi-crystalline Si solar cells with excellent results, up to 18.51% in conversion efficiency, have been achieved. Moreover, to further understand the model, effects of the firing temperature and the thickness of SiN_x layer on the contact-resistance have been investigated in the solar cells. It is proved that the formation of the silver crystallites is related to the existence of SiN_x layer.

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1. Introduction

In the production process of crystalline silicon solar cells, a thin layer of SiN_x is deposited on the textured emitter in order to passivate the dangling bonds and reduce the light reflection. After the deposition step, screen-printing of silver paste, followed by a firing process, is widely used in the front electrode fabrication. In the firing process, silver particles in the paste grow together due to the driving force of the minimization of surface energy. At the same time, the SiN_x layer is etched through and an electrical contact is formed.

With the rapid development of processing technology in Si solar cells, emitters of higher and higher sheet resistance have been adopted for increasing the conversion efficiency of solar cells by reducing the minority recombination in the emitter areas. Previously, emitters of low sheet resistance (40–50 $\Omega/\square$) were widely used to achieve good contacts for industrial mass production of silicon solar cells. However, low sheet resistance leads to the electrical losses in the cell performance because heavy doping concentration could result in high recombination velocity [1]. The motivations to get high electrical performance promoted the development of the silver paste. Nowadays, a new type of commercial silver paste is available for the production of the solar cells with high sheet resistance emitters (80–90 $\Omega/\square$).

The performance of solar cells is significantly affected by the series resistance, one of the key parameters of solar cells. However, the series resistance strongly depends on the contact-resistance between the silver and emitter, and the effectiveness of the silver penetration. The contacts of the solar cells based on the fundamental of metal–semiconductor contacts were first investigated in some early studies [2–5]. In the metal–semiconductor contacts, the conduction mechanism depends on the doping concentration (N_D) of the semiconductor substrate. For $N_D > 1 \times 10^{19}$ cm^{-3}, the field emission (FE) is dominant. For $N_D < 1 \times 10^{17}$ cm^{-3}, the thermionic emission (TE) is dominant. For 1×10^{17} cm$^{-3} < N_D < 1 \times 10^{19}$ cm^{-3}, it is a combination of TE and FE, defined as the thermionic field emission (TFE). In the recent research works [6–9], silver crystallites were observed in the interface layer between the silicon emitter and the silver fingers. It is believed that silver crystallites played an important role in the contact formation and current transport. Most of these results are based on mono-crystalline silicon, while the silver crystallites, with shape of inverted pyramid and penetrating into the silicon, are believed to be metal–semiconductor ohmic contact to the emitter [10].

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Although the contacts between the silver finger and the silicon emitter have been investigated widely, it is still difficult to give a completely clear picture of the formation of the Ag/Si contact due to: (a) the unclear current transport mechanism [11], (b) the formation mechanism of the silver crystallites [12], especially during the complexities of the latest commercial silver paste, (c) the textured surface topography and (d) the uncertainty of crystal orientation [13] in multi-crystalline silicon are taken into account. Based on the experimental and theoretical studies, here presents a detailed investigation on the contacts in the multi-crystalline silicon solar cells.

2. Experimental

156 × 156 mm^2 p-type industrial multi-crystalline silicon wafers, with bulk resistivity of 1–3 Ω cm, were used in the fabrication of the samples in a typical process of five steps, using the industrial production facilities. Step 1, the wafers were first textured or saw damage-etched by acid etching using a mixture HNO_3/HF system. Step 2, the n-type emitter was formed by the $POCl_3$ diffusion. Step 3, the rear junction and phosphosilicate glass were removed by a standard wet-chemical step. Step 4, the SiN_x antireflection and passivation layer was deposited via plasma-enhanced chemical vapor deposition (PECVD). Step 5, the front and back metallization process was carried out by screen-printing commercial silver and aluminum pastes, respectively. After the printing, the front and back contacts were simultaneously formed during a fast firing process in an IR heated belt furnace. In our studies, the commercial silver paste (Giga 590A), suitable for high sheet resistance emitters (80–90 Ω/□), was used for the front contacts. Two series of the samples were prepared in the experiment: (a) after conventional texturing, wafers diffused with emitters of different sheet resistances (56.4 Ω/□, 66.1 Ω/□ and 87.7 Ω/□ with the diffusion times 28 min, 20 min and 12 min, respectively) and coated with (without) a thin layer of 80 nm SiN_x were printed with four short silver fingers at the central region. The contact area is 3 × 0.06 mm^2 for each short finger and the spacing is 1.73 mm. (b) Solar cells with different SiN_x layer thicknesses (0 nm, 80 nm, 160 nm, 240 nm, 320 nm, 400 nm, 480 nm and 560 nm) were prepared with different firing temperatures (745 °C, 775 °C, 805 °C, 835 °C and 865 °C), respectively.

The sheet resistance of the wafers and the electrical performance of the solar cells were tested using 4-point probe method after step 3 in the processing, while the electrical performance of the solar cells was characterized with *I–V* tester after the step 5. The contact-resistance was measured using a 2-point and 4-point probe method. Field-emission scanning electron microscopy (SEM) was used to study the microstructure of the Ag/Si contact and energy dispersive X-ray spectrometry (EDX) was used to identify the Ag content of the micro-crystallites of the samples.

3. Results and discussion

3.1. Phosphorus diffusion in the textured wafers

Before studying the contact-resistance between the fingers and the emitter, the relationship between sheet resistance and phosphorus diffusion profile in the textured silicon wafers was first examined by theoretical simulation. According to the diffusion theory [14], the phosphorus diffusion in the industrial productions can be approximated to a model of constant source diffusion. The diffusion concentration can be written as follows:

$$N(x,t) = N_s\, erfc\frac{x}{2\sqrt{Dt}} = N_s \int_z^{\infty} e^{-z^2} dz \tag{1}$$

where

$$z = \frac{x}{2\sqrt{Dt}} \tag{2}$$

with N_s being the surface concentration, D the diffusion coefficient, x the depth and t the time. The diffusion coefficient changing with diffusion temperature can be written as follows:

$$D = D_0 \exp\left(-\frac{E_a}{kT}\right) \tag{3}$$

where D_0 is a pre-exponential constant, E_a is the activation energy, T is the temperature of diffusion, and k is the Boltzmann coefficient. According to the semiconductor theory [15], the sheet resistance ($dR_{\square}(x)$) of a thin layer (dx) at the depth x can be written as follows:

$$dR_{\square}(x) = \frac{\rho}{dx} = \frac{1}{\sigma dx} = \frac{1}{nq\mu_n dx} = \frac{1}{N(x)e\mu_n dx} \tag{4}$$

where μ_n is the mobility of the electron and can be written as an empirical equation [16].

$$\mu_n = 65 + \frac{1265}{\left(1 + \frac{N(x)}{8.5\times 10^{16}}\right)^{0.72}} \tag{5}$$

So, the total sheet resistance ($R_{\square}$) in the phosphorus diffusion emitter can be written as follows:

$$\frac{1}{R_{\square}} = \int \frac{1}{dR_{\square}(x)} = \int N(x) e\mu_n dx \tag{6}$$

In the simulations, D_0=3.85 cm^2/s, E_a=3.15 eV, and T=1093 K. According to Eqs. (1) and (6), the profiles of the phosphorus diffusion in the emitter can be simulated numerically by spreadsheet software. Fig. 1 shows the correspondence of sheet-resistance to the profiles of the phosphorus diffusion in the emitter. The simulated sheet resistances with diffusion times of 28 min, 20 min and 12 min are 56.7 Ω/□, 67.1 Ω/□ and 86.6 Ω/□, respectively, consistent to the experimental values of 56.4 Ω/□, 66.1 Ω/□ and 87.7 Ω/□, respectively.

In the former studies [17,18], it is known that silver paste can etch silicon with the result of silver crystallites penetrated into the

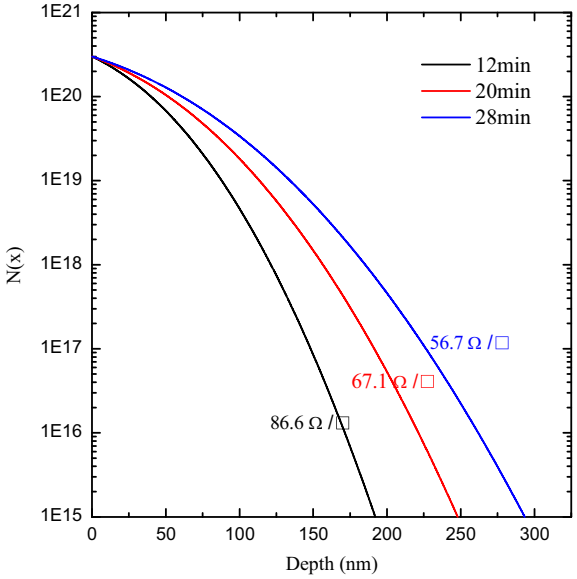

Fig. 1. Correspondence of sheet-resistance to the profiles of the phosphorus diffusion in the emitter simulated with different diffusion times of 28 min, 20 min and 12 min at temperature of 1093 K.

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