Improvement of Silicon Solar Cell Metallization with Printed Metal Nanoparticle Ink

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ABSTRACT

In this paper we will present two approaches for the frontside metallization of crystalline silicon solar cells, targettting on dramatically reducing the specific contact resistance between the metal gridline and the n+ emitter layer. The first one is to use a blanket sputtered Ni film as the contact layer and screen printed Ag lines as an etch mask to pattern the underlying Ni film. The experimental result shows that, the specific contact resistance with this approach can be reduced by almost two orders of magnitude compared to only using screen printed Ag gridlines. In order to further reduce the cost for introducing the Ni contact layer, using inkjet printed Ni nanoparticle ink to form the contact layer is also studied. It has been shown that, with well controlled printing and annealing conditions, the printed Ni ink approach can achieve almost the same contact resistance as that using sputtered Ni film. The signficant reduction on contact resistance can increase the absolute cell efficiency by up to 0.9%, according to the PC1D modeling result.

Keywords: silicon solar cells, contact resistance, nanoparticle ink, metallization, nickel

1 INTRODUCTION

Currently about 85% of the solar photovoltaic cells produced worldwide are based on crystalline silicon wafers. Front side metallization is one of the most critical process steps for conventional silicon solar cells. The most widely used method at present is to screen print Ag gridlines on top of the silicon wafer coated with a silicon nitride antireflection layer, then fired at high temperatures (around 800ºC) which allows the Ag lines to penetrate through the nitride layer to form the contact with the n+ emitter layer. While this screen printing fire through process has the advantages of robust, low cost, and high throughput, it also produces a poor, very resistive metal-silicon contact, which significantly limits the cell efficiency[1]. Generally, the specific contact resistance of fired-through silver lines is in the range of 3 to 10 mohm·cm^2, which is about four orders of magnitude higher than that used in semiconductor industry (at the order of 10^{-7} mohm·cm^2)[2]. To compensate this large specific contact resistance, large contact area and the emitter layer with low sheet resistance have to be used, which decreases the cell efficiency.

Forming a silicide metal contact layer (e.g., NiTi) has been proved to be a robust approach to achieve the metal-silicon contact with very low specific contact resistance in semiconductor industry [3]. In the first part of this paper, we will demonstrate that by using a high quality sputtered Ni film as the contact layer, the specific contact resistance can be reduced by about two orders of magnitude. Then we will demonstrate by using inkjet printed Ni nanoparticle ink can get almost the same contact resistance as that using sputtered Ni film, with well controlled printing and annealing process conditions. As the inkjet printed approach is an inline process and have much lower cost, it is very promising to be implemented in the solar cell production line.

2 METALLIZATION APPROACHES

Sputtered metal films, with the metal material which can form silicide compounds with silicon such as Ni, Co, and Ti, have been extensively used in the semiconductor industry and can have very low specific contact resistance with silicon (on the order of 10^{-7} $\Omega\cdot$cm^2) and robust adhesion to the silicon substrate with very low stress. However, these sputtered metal films generally have to be patterned using a photolithographic process, which is very difficult to be implemented in solar cell manufacturing due to the intrinsic high cost and complexity of photolithography. Hence in our first approach we will use a sputtered Ni film to form the contact layer, but we propose using the screen printed Ag gridlines as an etch mask to pattern the underlying sputtered Ni film. This also makes the Ni contact layer self-aligned with the Ag gridlines and permits immediate cell testing after firing.

The basic procedure of the approach is shown in Fig. 1. Starting with a solar cell silicon substrate (a) and after drilling the contact holes through the nitride layer using laser ablation method (b), a thin Ni film is sputtered on the whole surface (c), followed by screen printing Ag gridlines which are aligned with the contact holes (d). Next the uncovered Ni film is etched away using the Ag gridlines as a protective mask, then the Ag gridlines and the underlying Ni contact layer are co-fired at high temperatures to finish the metallization, as shown in Fig. 1(e).

When using inkjet printed nickel nano ink approach, the step (e) will be replaced by an inkjet process which directly prints the nickel nano ink into the contact openings, and followed by step (d) – screen printing silver lines. Then in step (e), the etching process is not needed and directly goes to co-firing process.

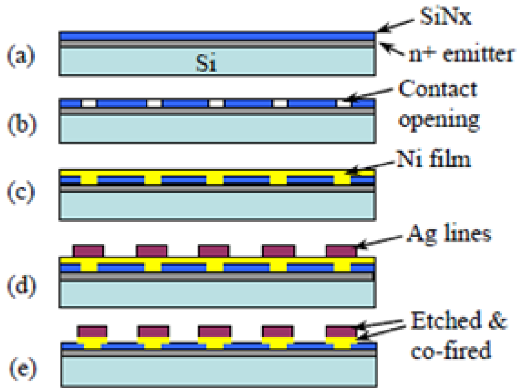

Figure 1. Metallization procedure using sputtered Ni film as the contact layer

3. RESULTS AND DISCUSSIONS

3.1. Sputtered Ni Approach

The pecific contact resistance with sputtered Ni approach was characterized first. In order to simplify the experiment and as a first step to verify the possibility of the new metallization method shown in Fig. 1, we use a polished, arsenic heavily-doped, 0.50 mm-thick silicon wafer with the bulk resistivity of about 0.0015 Ω·cm, hence the whole silicon wafer functionally substitutes for the n+ emitter in the solar cells (with 50 Ω/□ sheet resistance and 0.3 to 0.4 µm layer thickness, the emitter layer is equivalent to a bulk resistivity of 0.0015 to 0.002 Ω·cm). The silicon wafer is covered by an 80 nm thick PECVD SiN_X dielectric layer.

The sample size is about 38.1 mm (1.5”) x 38.1 mm. To measure the contact resistance using the Transmission Line Method (TLM), first seven lines of contact holes with diameter of about 35µm in the nitride layer were laser drilled. The spacing between the adjacent lines varies from 2.0 mm to 7.0 mm, with the step of 1.0 mm. In each line the distance between adjacent holes is about 0.254 mm and the line length (from the first opening to the last opening) is about 25.4 mm (1”), and hence 100 contact holes were drilled in each line. The laser drilling method and condition was reported in an earlier paper [4]. After laser drilling the contact holes, a 100 nm-thick Ni film was blanket sputtered, followed by screen printing Ag gridlines which were aligned with the lines of contact holes. The Ag paste used is Ferro CN33-462. Then the sample was dropped to a $FeCl_3$ solution to etch away the uncovered Ni film. After patterning the Ni film the Ag gridlines along with the underlying Ni contact layer (called as Ag/Ni lines) were co-fired at 500°C using a rapid thermal annealer (RTA). Then the I-V curve between the adjacent Ag/Ni lines was measured using the four probe Kelvin method, from which the resistance value was derived, and then the resistance between the adjacent Ag/Ni lines vs. the line spacing was plotted.

Shown in Fig. 2(a) is a typical I-V curve with the line spacing of 4.0mm. The very straight linear line indicates the excellent ohmic contact between Ag/Ni electrode and the silicon substrate. The reciprocity of the slope represents the resistance between these two adjacent lines. Fig. 3 gives the dependence of the resistance measured between the adjacent Ag/Ni lines on the line spacing.

For our sample the total resistance R_T between the Ag/Ni lines is the sum of the contact resistance R_C between the Ni contact layer and the underlying Si plus the Si substrate resistance R_{Si} between the Ag/Ni lines, and can be expressed as:

$$R_T = 2R_C + R_{Si} = 2R_C + \rho_{Si} d/(L \cdot t)$$

Where ρ_{Si} is the Si substrate resistivity, d is the line spacing, L is the line length, and t is the substrate thickness. Putting the numbers for each parameter in the equation we found that the silicon substrate resistance R_{Si} is about

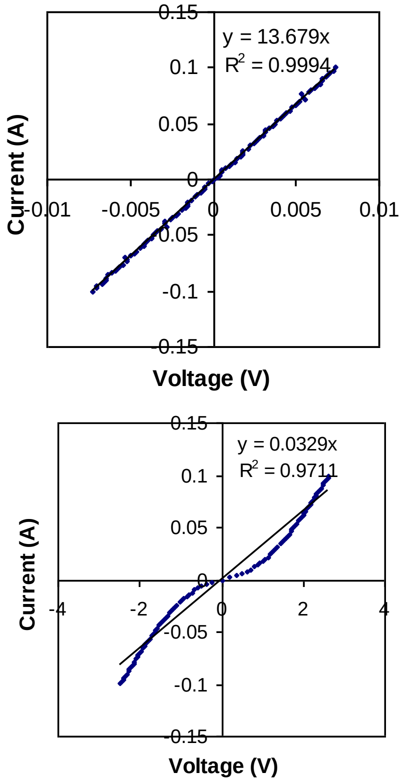

Figure 2. Typical I-V curves between adjacent, 4mm separated Ag/Ni lines for the sample (a) having laser drilled holes and (b) no laser. drilled holes.

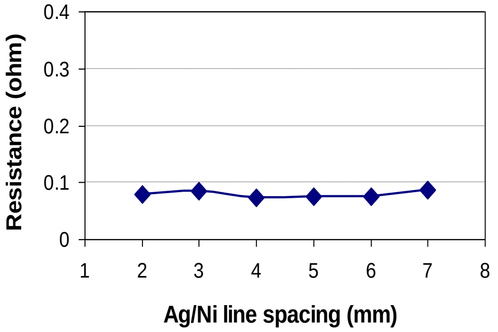

Figure 3. Resistance between adjacent Ag/Ni lines vs. line spacing

0.0077Ω for the 7mm line spacing. This is about one order of magnitude smaller than the measured resistance R_T which is between 0.073 and 0.087Ω. Hence in our case the measured resistance R_T is mainly contributed by the contact resistance R_C and should be almost not related to the line spacing, which is consistent with the experimental data shown in Fig. 3. Thus the above equation can be simplified to $R_T \approx 2R_C$, from which R_C can be derived. Then considering the contact is through the laser drilled holes the contact area can be calculated, and finally the specific contact resistance can be obtained. Through these calculations we got the specific contact resistance is around 0.04 mohm·cm^2. This is about two orders of magnitude smaller than the specific contact resistance formed by using the fired-through silver gridlines and the n+ emitter layer, which is generally between 3 to 10 mohm·cm^2.

In order to confirm all the contacts are through the laser drilled contact holes and no possibility of firing through nitride layer by the Ag/Ni lines. Another sample was prepared by the same procedure but no laser drilled contact holes, and the I-V curves between the adjacent Ag/Ni lines were measured, with a typical result shown in Fig. 2(b). The complicated shape of the I-V curve, and the more than 400 times higher resistance than Fig. 2(a), indicates that it is impossible for the Ag/Ni lines to fire through the nitride layer and to form a good contact with low contact resistance.

3.2. Inkjet Printed Ni Nano Ink Approach

In order to develop an inline, vacuum-free process which is most cost effective and more easily implmented in the curren solar cell production line, it is expected that the sputtered Ni contact layer can be simply replaced with an inkjet printed Ni ink layer. The key question is if an inkjet printed Ni ink layer can get to the similar contact resistance that the sputtered Ni film achieved, which is the experimental work in this section focused on.

In order to make the exact "apple to apple" comparison and also simplify the experiment, we took the same silicon substrates (coated with the nitride layer) and made the contact holes under the same laser ablation condition. Then the samples were divided into three groups: for the 1st group we only screen printed seven lines Ag paste which covered the seven lines of contact holes and then cured at 200°C. The 2nd group samples were covered with sputtered Ni film, followed by patterning and annealing, and then the Ni lines were covered with the same screen printed Ag lines as the 1st group samples. For the 3rd group samples we inkjet printed Ni nanoparticle ink into the contact openings. These formed seven inkjet printed Ni lines which covered the corresonding the seven lines of contact holes. Then the Ni printed lines were annealed under different conditions. After annealing the samples were screen printed with the same Ag lines as the 1st group samples. The Ag lines for the 2nd and 3rd group samples were mainly used to increase the metal line conductivity, so that the I-V transmission line measurement between the metal lines can be carried out correctly. After the I-V measurement, we took the average of the resistance between the adjacent metal lines, which can be considered as 2 times of the contact resistance, according to the discussion in last section.

The contact resistance data for different groups of samples are given in Fig. 4. The group with only screen printed Ag paste lines show very high contact resisance, indicating the Ag paste cannot form a good contact with silicon, hence any contact resistance reduction for 2nd and 3rd group samples must come from the Ni contact layer. The sputtered Ni film has very small contact resistance data, which is consistent with the experiment in last section. For the samples with inkjet printed Ni nanoparticle ink, we found the contact resistance is very sensitive to the drying and annealing conditions after printing.

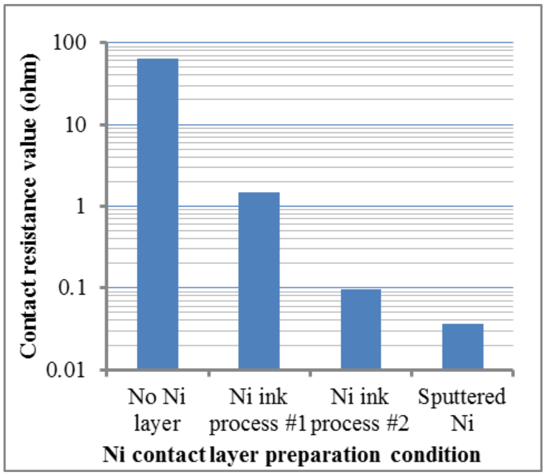

Figure 4. Measurely contact resistance values for diffrently processed Ni contact layer.

When the drying and annealing conditions were not processed correctly (named as Process #1), after annealing the printed Ni layer cannot have a good adhesion to the Si substrate, and the Ni layer can only partially react with silicon and form a Ni silicide contact, as shown in Fig. 5(a). While this can make the contact resistance much smaller than that only using silver paste, which didn't form any Ni silicide contact at the metal silicon interface, but still much larger than that using sputtered Ni film, which can be considered as almost fully convered with Ni silicide contact. With further improvement on the drying and annealing conditions (named as Process #2), after annealing the printed Ni layer can have a good adhesion to the silicon substrate and form a Ni silicide contact along almost all the metal-silicon contact area, as shown in Fig. 5(b). This leads to the contact resistance with printed Ni ink very close to that with sputtered Ni film, as shown in Fig. 4.

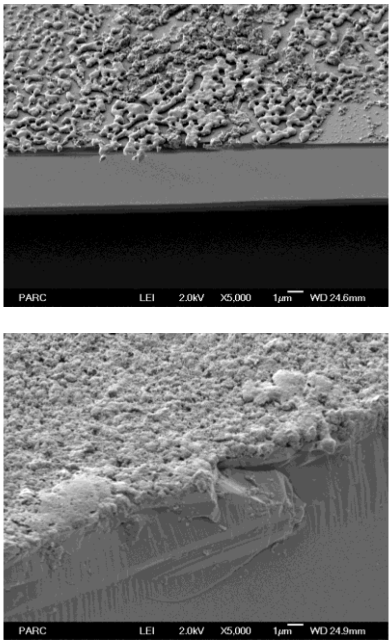

Figure 5. Printed Ni layer morphology after annealing with: (a) process #1; (b) process #2

3.3. Efficiency Improvement

The significant reduction in specific contact resistance in our new approaches can improve the cell efficiency in three aspects: 1). the contact area between the front side electrode and the n+ emitter layer can be reduced, which reduces the front side recombination velocity; 2). The resistance of Ag gridlines can be reduced by reducing the glass frit content in the Ag paste or even using frit-free Ag paste, as the firing-through is not required by using laser drilled contact holes; 3). Emitter layer with higher sheet resistance (e.g., 100 Ω/□ instead of 50 Ω/□) can be used, which improves the short-wave length response. We have simulated the improvement of each of these factors by using PC1D software, and the results are given in Table 1, where "0" represents the baseline which uses the fire-through Ag paste process and the cell efficiency is 17.1%, and "1" represents the improved situation by using our technology. It can be seen that totally about 0.9% absolute efficiency improvement can be reached.

F SRV	R_s	Emitter	Eff. (%)	Increase
0	0	0	17.1	Baseline
0	0	1	17.4	0.3
0	1	0	17.2	0.2
0	1	1	17.6	0.5
1	0	0	17.5	0.4
1	0	1	17.8	0.7
1	1	0	17.7	0.6
1	1	1	18.0	0.9

Table 1. Efficiency improvement modelled by using PC1D software

In solar cell industry, the added cost of the new technology for per added watt of power due to the efficiency improvement (defined as incremental cost) is a critical factor to consider when implementing the new technology. Our cost analysis indicates that for the sputtered Ni approach, the incremental cost per added watt is $0.74/Wp. When inkjet printed Ni is used, the cost can be dramatically reduced due to get rid off the vacuum sputtering process and the etch step, which leads to the incremental cost is only about $0.12/Wp. Hence the inkjet printed Ni approach would be very attractive for solar cell industry.

4. CONCLUSION

We have demonstrated two different approaches to form a Ni contact layer which can significantly reduce the specific contact resistance for crystalline silicon solar cells: sputtered Ni with screen printed Ag gridlines as etching mask and inkjet printed Ni nanoparticle ink. The sputtered Ni approach can reduce the specific contact resistance by about two orders of magnitude compared to the conventional fire through Ag paste method. With well controlled process conditions, the inkjet printed Ni ink approach can have the contact resistance very close to that using sputtered Ni film. The significant reduction in specific contact resistance can increase the absolute cell efficiency by about 0.9%. Due to the inline process nature and extremely low incremental cost per added watts, the inkjet printed Ni nano ink approach should be very attractive to solar cell industry.

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