ABSTRACT

Selective removal of the silicon nitride dielectric layer has been demonstrated even using nanosecond range laser pulses, through carefully controlling the energy density of laser pulses. It has been found that, a laser pulse with a peak energy density of 4.3 J/cm² or lower can remove the nitride layer without altering the underlying silicon while a pulse with a peak energy density of 4.8 J/cm² or higher will substantially damage the silicon. With the laser energy density maintained below the threshold for silicon ablation, multiple laser pulses can be used to more completely remove the nitride layer. Also, using high quality blanket sputtered nickel film as metal contact layer and screen printed silver gridlines as an etching protection mask, a new method for front side metallization has been developed. The specific contact resistance can be reduced by about two orders of magnitude compared to the conventional screen printed and fired through silver contact, and the firing temperature can be lowered to about 500°C.

INTRODUCTION

While screen printing silver paste and firing through the silicon nitride dielectric passivation/antireflection layer is the most widely used front side metallization method for silicon solar cells, it is also one of the major factors limiting cell efficiency, mainly due to producing a poor, very resistive metal-silicon contact [1]. Several alternatives to replace screen printed silver metal contact have been studied in the past decade, among which using laser ablation to generate contact openings in the silicon nitride layer followed by a suitable metallization process has received the most extensive study [2].

Laser ablation has many advantages such as being clean (dry method), simple (no mask needed), non-contact, and fast. To utilize this technology for front side metallization of silicon solar cells, at least two questions need to be answered: first, if selective removal of the silicon nitride layer can be achieved without damaging the underlying emitter layer; second, how to form the metal contact layer and metal gridlines after forming the contact openings.

Several groups have reported the possibility of selective ablation of the silicon nitride layer, but the laser beam conditions are not consistent [2-5]. Some reports show that very short (picosecond) or ultra short (femtosecond) laser pulses are needed, which makes it more difficult for commercialization [4,5]. Also it is not clear how to completely remove the silicon nitride in the opening areas.

A number of methods for forming the metal contact with the n+ emitter layer after making the laser ablated openings have been proposed. Ink jet printing nanophase contact metal solutions into the openings seems to be the most elegant approach [6]. However due to technical difficulties so far there is no successful experimental result reported. Electroless plating nickel to form the contact layer, followed by electroplating silver or other metal layer to form gridlines has been broadly studied [7]. However, it is still a big challenge to form a high quality, continuous and dense nickel contact layer through electroless plating, as well as to achieve high throughput for mass production.

In the first part of this paper we will demonstrate that, by carefully controlling the energy density of the laser pulses, selective removal of the silicon nitride dielectric layer can be achieved even using nanosecond range laser pulses. Moreover, maintaining the laser energy density below the threshold for silicon ablation, multiple laser pulses can be used to more completely remove the nitride layer. In the second part of this paper, a new method for metallization is presented, which uses a blanket sputtered nickel film as the metal contact layer and screen printed silver gridlines as an etch mask to pattern the underlying nickel film. Compared to the conventional fired through silver contact, the new method can reduce the specific contact resistance by about two orders of magnitude.

SELECTIVE REMOVAL OF SILICON NITRIDE DIELECTRIC LAYER

Experimental

A customized laser micromachining system made by PhotoMachining Inc. is used in this work. The laser source is a quadrupled Nd:YAG Coherent AVIA laser with 266nm wavelength. The sketch of the optical system is shown in Fig. 1, and a galvo scanner is used to drill the contact openings on the samples. The distance between the focal lens and the surface of the sample, which is defined as stage height by the control software, can be easily adjusted by changing the position or height of the focal lens. This also changes the laser spot size on the surface of the sample, with smallest spot size reached when the sample surface is at the focal position. Hence for a given
laser beam energy, we can change the energy density through changing the laser spot size, which can be done by adjusting the stage height.

In order to easily characterize the profiles of the laser drilled contact openings, in this paper we use polished silicon wafers with an 80nm thick PECVD silicon nitride dielectric layer. The silicon wafer is heavily arsenic doped with a 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).

Results and Discussion

For this work we have fixed the laser beam energy at 93 µJ/pulse, with a pulse length of 20 ns and a repetition rate of 30 kHz. The galvo scan speed is 7620 mm/s, which gives the spacing of 0.254 mm between openings. We have changed the stage height from 84.7 mm to 94.7 mm, with the step of 0.50 mm. With the stage height of 88.7 mm, the laser beam is focused on the sample surface. As the stage height is moved away from this value, the laser beam becomes more defocused, the spot size larger, and the pulse energy density incident on the substrate smaller.

At each stage height we drill a series of contact openings, or simply called holes in this section, and measure the hole profiles using a Dektak stylus profilometer, based on which the hole depth is determined. Fig. 2 shows a plot of hole depth as a function of stage height, and Fig. 3 shows the optical micrographs of the laser drilled holes at some stage heights.

It can be seen from Fig. 2 that when the stage heights are from 84.7 mm to 85.2 mm, the hole depths are from about 83 nm to 100 nm, which means the nitride layer is ablated away. From Fig. 3 it can be seen that there is no damage or significant melting of the silicon substrate. However, when the stage height increases to 85.7mm, the hole depth suddenly increases to about 490nm, and also melting and freezing of liquid Si capillary waves on the silicon substrate can be clearly observed from Fig. 3. When the stage height increases from 85.7 mm to 88.7 mm, the focal position, the hole depth gradually increases while melting of the silicon substrate increases. After passing the focal position, for the stage height from 88.7 mm to 91.7 mm, the hole depth and melting of Si gradually decrease. When the stage height increases from 91.7 mm to 92.2 mm, the hole depth suddenly decreases from 527 nm to 97 nm, and also there is no significant melting of the silicon substrate. As the stage height further increases to 94.2 mm, the hole depth is only about 44 nm, which does not penetrate through the nitride layer.

These results demonstrate that when the stage height is from 85.7 mm to 91.7 mm, or within ± 3.5 mm from the focal position (the focus position is 88.7mm), the laser drilled holes will substantially penetrate into the silicon
substrate and cause damage or melting. However, when the sample is more than 3.5 mm away from the focal position, the silicon nitride layer can be ablated without visibly damaging the underlying silicon substrate. This clearly indicates that there is a threshold for the energy density where the silicon nitride layer can be removed without altering the underlying n+ silicon emitter layer.

In order to more accurately determine this energy density window, the sample position is more precisely adjusted and the positions where the underlying silicon is not damaged and starts to be damaged are determined. The beam powers at the surface of the sample at these two positions are measured using a laser power meter with a 35µm aperture. Then by approximating the beam shape as Gaussian function the energy profiles of these laser pulses are calculated. The results are given in Fig. 4. It indicates that the underlying silicon layer will not be damaged with the peak energy density up to 4.3 J/cm², and will start to be damaged with the peak energy density of 4.8 J/cm². To remove the nitride layer the energy density needs to be at least 0.5 J/cm².

One of the challenges using laser drilled contact openings is that silicon nitride removal by a single sub-threshold pulse is incomplete, and this reduces the contact area. In this work we have found that, when the laser energy density is maintained below the threshold for silicon ablation, multiple laser pulses can be used to more completely remove the nitride layer. The micrographs of the laser drilled holes with different pulses are shown in Fig. 5, the hole profiles are shown in Fig. 6, and the EDS nitrogen maps are given in Fig. 7. These results clearly demonstrate multiple laser pulses can more completely remove the nitride layer, without substantially increasing the hole depth or damaging the underlying silicon. We have found even after 100 laser shots the silicon substrate is still not considerably damaged.

The doping profiles in the holes with different pulses, and in the area without holes, were measured using SIMS and the results are shown in Fig. 8. Fig. 8(a) gives the element analyses at the area without holes, which shows a normal nitride layer on the top of As-doped silicon. Fig. 8(b) shows the results at the hole areas. However as the scan area is always larger than the hole area, the results also contain some noise level of silicon and nitride. Nevertheless the results clearly demonstrate the more removal of nitrogen for two pulses than one pulse. More importantly, comparing to Fig. 8(a) it can be found the As doping in the silicon is not changed, no matter one or two pulses are used.
METALLIZATION USING SPUTTERED NICKEL FILM

Description of the Method

Forming a good metal contact layer is another challenge to use laser drilled contact openings for front side metallization. Sputtered metal films, especially the metals which 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 $10^{-7} \, \Omega \cdot \text{cm}^2$) and robust adhesion to the silicon substrate with very low stress. However, these sputtered films generally have to be patterned using a photolithographic process, which will increase the cost of solar cells manufacturing. In this paper we propose using screen printed silver gridlines as an etch mask to pattern the underlying sputtered nickel contact layer. This approach ensures the use of high quality nickel film as a contact layer to reduce the contact resistance, and also avoids the use of standard photolithographic process to reduce the cost. In addition, it makes the nickel contact layer self-aligned with the silver gridlines and permits immediate cell testing after firing.

The basic procedure is described in Fig. 9. Starting with a solar cell silicon substrate (a) and after drilling the contact openings through the nitride layer (b), a thin nickel film is sputtered on the whole surface (c), followed by screen printing silver gridlines which are aligned with the contact openings (d). Next the uncovered nickel film is etched away using the silver gridlines as a protective mask, then the silver gridlines and the underlying nickel contact layer is co-fired at high temperatures to finish the metallization, as shown in Fig. 9(e).

Results and Discussion

In order to simplify the experiment and as a first step to verify the possibility of the new metallization method shown in Fig. 9, again we use polished, heavily arsenic doped, 0.50 mm-thick silicon wafer with the bulk resistivity of about 0.0015 $\Omega \cdot \text{cm}$, covered by an 80 nm thick PECVD silicon nitride dielectric layer. The experiment on the textured, solar cell-type silicon substrates is being conducted and the results will be reported separately.

The sample size is about 38.1 mm ($1.5\) \times 38.1 \text{ mm}$. In order to measure the contact resistance using the Transmission Line Method (TLM), first seven lines of contact openings 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 openings varies from 2.0 mm to 7.0 mm, with the step of 1.0 mm. In each line the distance between adjacent openings is about 0.254 mm and the line length (from the first opening to the last opening) is about 25.4 mm (1''), hence 100 contact openings were drilled in each line. After drilling the contact openings, a 100 nm-thick nickel film was blanket sputtered, followed by screen printing silver gridlines which were aligned with the lines of contact openings. The silver paste used is Ferro CN33-462. A photograph of the sample at this stage is shown in Fig. 10(a). Then we dropped the sample in a ferric chloride etching solution for about 5 seconds, the uncovered nickel film was removed, without any damage of the silver gridlines, as shown in Fig. 10(b). This verifies the success of patterning the sputtered nickel film using silver gridlines as the etch mask.
After patterning the nickel film the silver gridlines along with the underlying nickel contact layer, which we call 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 and the line spacing was plotted.

Shown in Fig. 11(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. 12 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 nickel contact layer and the underlying silicon plus the silicon 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 $\rho_{Si}$ is the silicon substrate resistivity, d is the line spacing, L is the line length, and t is the substrate thickness. Putting the numbers for each parameter we found that the silicon substrate resistance $R_{Si}$ is about 0.0077 $\Omega$ 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 0.087 $\Omega$. 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. 12. 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 openings 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·cm². This is about two orders of magnitude smaller than the specific contact resistance between the fire-through silver gridlines and the n⁺ emitter layer, which is usually between 3 to 10 mohm·cm².

In order to confirm all the contacts are through the laser drilled contact openings 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 openings, and the I-V curves between the adjacent Ag/Ni lines were measured, with a typical result shown in Fig. 11(b). The complicated shape of the I-V curve, and the more than 400 times higher resistance than Fig. 11(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.

To further characterize the contact of this fired Ag/Ni lines with silicon substrate Schottky diode samples were prepared on a lightly doped silicon substrate with the resistivity of about 0.5 $\Omega$·cm, and the structure is shown in Fig. 13. The forward bias characteristic (I-V curve) was measured under three different conditions, and the results are given in Fig. 14: (1) after sputtering the Ni film and prior to screen printing Ag paste; (2) after firing the Ag/Ni line at 500°C in air; and (3) after firing the Ni film at 500°C in air without Ag coverage.

We have found that the bare Ni film was severely oxidized after firing, and this greatly changed the I-V characteristic of the diode, as shown in Fig. 14. However, when covered by the Ag paste the Ni film was not oxidized after firing and the I-V characteristic was almost not changed. This is probably because the Ag paste coverage provides the protection, and more importantly, the
decomposing organics in the Ag paste generated a localized reducing or oxygen-deficient atmosphere.

The linear part of the I-V curve follows the thermionic emission mechanism and can be expressed as [8]:

\[ I = A \cdot A^* \cdot T^2 \cdot e^{-\frac{\Phi_B}{kT}} \cdot e^{\frac{qV}{n kT}} \]

Where A is the diode area, A* is Richardson constant, \(\Phi_B\) is the barrier height, and n is ideality factor, which ideally should be equal to unity. Through fitting into the above equation, the barrier height and ideality factor after sputtering Ni and after firing Ag/Ni lines are calculated, and given in Table 1, along with the reported barrier height for Ni/Si and NiSi (nickel silicide)/Si junction [9].

After firing Ag/Ni lines the ideality factor is still very close to 1, verifying the silver paste and high temperature firing will not change the Ni/silicon interface. The slight increase of the barrier height after firing may indicate the formation of some nickel silicide. All these results demonstrate the fired Ag/Ni lines have the similar contact characteristic with silicon as Ni film or nickel silicide used in semiconductor industry, and hence very low contact resistance can be obtained.

It is worth to point out that the Ni film also enhances the adhesion of the Ag gridlines. The firing temperature of the paste we used, Ferro 33-462, is around 800°C. When fired at 500°C directly on the nitride layer, it doesn’t have any adhesion and will be peeled-off after firing. However, with the underlying Ni layer the Ag lines can have strong adhesion to the substrate after firing at 500°C.

### Table 1. Schottky barrier height and ideality factor

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<thead>
<tr>
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<th>Sputtering Ni</th>
<th>After firing Ag/Ni</th>
<th>Ni/Si reported</th>
<th>NiSi/Si reported</th>
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<td>(\Phi_B) (eV)</td>
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<td>0.60</td>
<td>0.61</td>
<td>0.67</td>
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<tr>
<td>n</td>
<td>1.02</td>
<td>1.01</td>
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**CONCLUSION**

In this paper we have demonstrated the selective removal of the silicon nitride dielectric layer using nanosecond range laser pulses, through carefully controlling the energy density of laser pulses. With a peak energy density of 4.3 J/cm² or lower the nitride layer can be removed without altering the underlying silicon, and multiple laser pulses can be used to more completely remove the nitride layer. A new metallization method using blanket sputtered nickel film as metal contact layer and screen printed silver gridlines as an etch mask is developed. It ensures the use of high quality nickel film as a contact layer to reduce the contact resistance and avoids the use of standard photolithographic process to lower the cost. The result shows the Ag/Ni lines can be co-fired at about 500°C with good adhesion to the silicon substrate, and the specific contact resistance is about two orders of magnitude lower than the conventional screen printed and fired through silver contact.

**REFERENCES**