ELECTROCHEMICAL DEPOSITION CONDITIONS OF GOOD COPPER CONTACT ON SILICON SOLAR CELLS

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Abstract

We have targeted in this study the contact deposition of copper on the silicon surface of a solar cell. We show the different drawbacks encountered in the process and present some solution and ways to obtain satisfactory copper-based contact. Nickel and copper are studied individually by varying the current density and the deposition time. The final structure obtained is a layer of 140 nm of nickel and more than 10 µm of copper. The quality of the contact strongly depends on the uniformity of the deposit. The thickness must be the same on each point of opened surface and the busbar that is 1.5mm wide has to be adequately fulfilled as the fingers that are narrower (less than 200µm). The adhesion is also an important parameter to make a good contact. If these conditions are completed the obtained contact resistance is around 1mΩ.cm². This condition implies a good seed layer of Ni, without oxidation. A heat treatment around 400°C during 5min in an inert atmosphere provides an accurate Ni seed layer. Otherwise the Cu top layer will comes off. So the conditions of a good contact deposition are tightly related to the surface preparation.

Keywords: Electrochemical deposition, copper contact, Si solar cells, adhesion

INTRODUCTION

Silicon is still the most used material in solar cells due to its electrical and mechanical properties. The challenge is to lower the cost of fabrication. One way is to replace the silver used in the front contact by a cheaper material like copper (Cu) and nickel (Ni). Cu and Ni cost a respectively 95 and 30 times cheaper than silver [1]. Furtherly, conductivity of Cu is equivalent to that of Ag (59.1 and 61.39 106 S/m) and density is 8.92, 10.49 respectively. The Ni/Cu structure can reduce the contact resistance to 1mΩ.cm² on silicon emitter [2].

Ni silicide has been used as material for contact to microelectronic CMOS devices [3,4]. Publications from microelectronic companies on NiSi contacts point out the practical advantages of this material which reside in a low thermal budget for formation, a low resistivity in narrow dimensions and a low device leakage [5].

Ni is used as contact barrier to copper and permits low contact resistance (Rc) on n+ silicon [6,7]. The deposition method also permits to reduce the cost by using the electrochemical plating rather than the usual screen printing.

1. EXPERIMENTAL PROCEDURE

A simple method for metal deposition on solar cells surface is used in this work. Ni chloride and Cu sulfide are used to deposit contacts on front surface. The pattern is obtained by laser ablation on silicon nitride. Laser treatment permits also to get a selective emitter n++ of 30Ω/□ sheet resistance on which Ni is first electrochemically plated. To get the Ni-Si phase, different temperatures are used to cure Ni deposited on Silicon and contact resistance is measured. Then Cu is selectively deposited on the Ni seed layer [7]. Ni-Si phase and Cu distribution are investigated using contact resistance measurement by TLM.

Globally the sequences of a the process for solar cell begin with a multicrystalline silicon wafer. Surface undergoes saw damage etch and cleaning. Diffused emitter of 60Ω/□ is obtained in POCl3 ambient using ‘Lydop technic”. After PSG removal a silicon nitride (SiNx) layer of 78 nm is deposited by PECVD. A layer of Al is screen-printed on the back side and fired. A 532nm pulsed laser is used to create heavily doped regions n++, opening in the same time a grid pattern through the SiNx layer to allow the selective deposition of Ni/Cu on the emitter.

Successive layers of Ni and Cu are electrochemically deposited on a silicon emitter to obtain the front grid contact and finalize the solar cell structure. The front contact is deposited in a bath of Ni containing NiCl2 as precursor element. The Cu is then deposited using a solution containing CuSO4. A final plasma or laser treatment is made to ensure edge isolation of the solar cell.

2. RESULTS

2.1 Laser ablation and emitter

The laser power and speed must be selected to ablate uniquely the SiNx layer without perturbing the underneath surface of the emitter. A particular attention must be paid to ablate the SiNx layer without letting a residual trace of SiNx; otherwise this will impede the metal deposition.

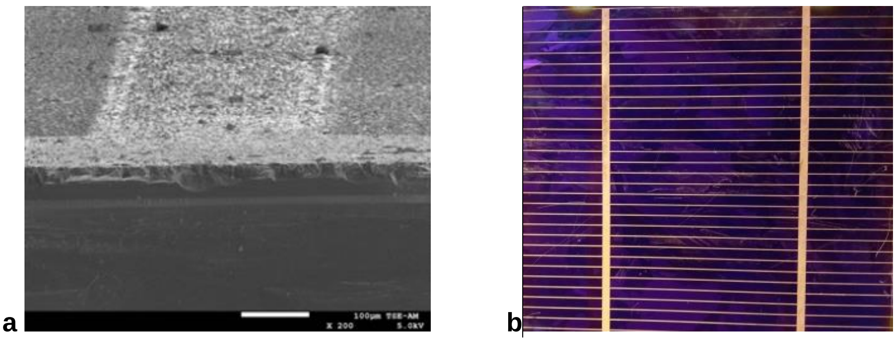

Figure 1 Image of ablated surface on SiNx (a) layer and cell with Cu contact (b)

The Ni/Cu deposit on the grid of the cell structure (140nm of Ni and 10 μm of Cu) is shown in **Figure 1**. The busbar is in the front of the image and the finger is in the back and perpendicular to the busbar.

2.2 The adhesion of Ni deposit and firing

It requires good cleaning of the surface from laser ablation residue. Then a few seconds of immersion in 10% HF allows to receive a deposit with good adhesion.

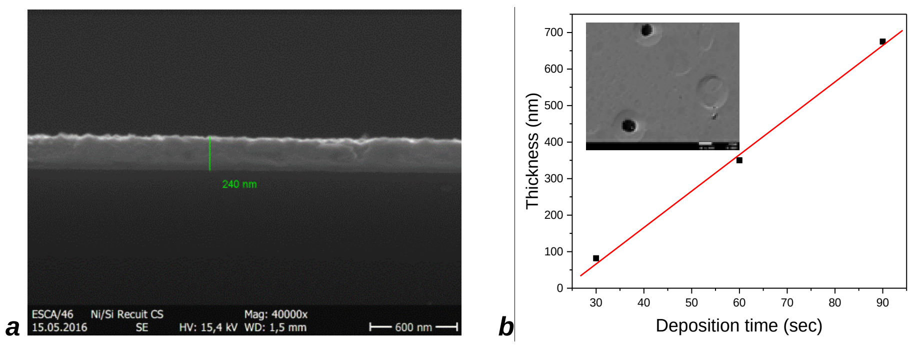

Figure 2 SEM image(a) of Ni layer and (b) Thickness of Ni vs deposition time (inset Ni layer showing pinholes)

The Ni is electrodeposited at low current density (I < 10mA/cm²) at temperature of 60°C. Than the film is fired to create a NiSix phase that serves as seed layer for Cu.

We obtain a linear rate of thickness with deposition time. 40 seconds of deposit allow a deposit of 140nm of Ni (**Figure 2**) that is enough to be used as seed layer. The deposit must be uniform without pinholes like seen on **Figure 2.a**. These latter are an opening for Cu penetration which would be harmful to the device. Firing at around 400°C creates detrimental pick up or debonding of Ni as seen inside of the frame of **Figure 3.a**. No seed layer prevents the Cu from being deposited on the substrate or will be a window for the diffusion of the Cu. Annealing carried out under an inert atmosphere and slow cooling prevents the Ni from detaching, or peeling off as confirmed by the tape test.

a *b*

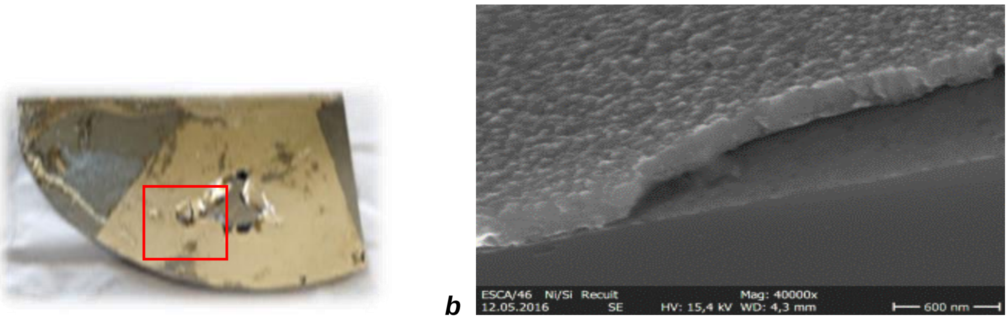

Figure 3 Optical image (a) and SEM image (b) of Ni layer after annealing at 400°C

2.3 Copper deposition

A layer of several microns of Cu is necessary to finalize the front contact of the cell. SEM micrographs of the Cu deposited at low current with less than10mA/cm² and at high current with greater than 40mA/cm² are shown in **Figure 4**.

a b c d

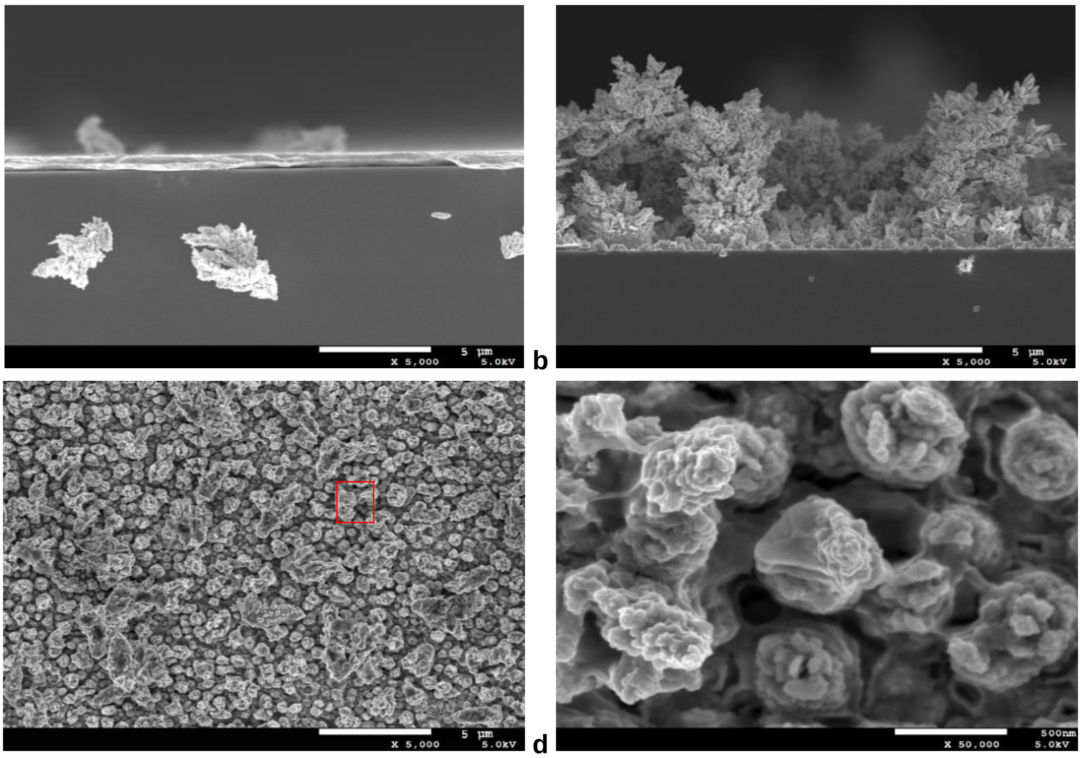

Figure 4 SEM imaging of the Cu deposited, Cross-section Image a) at low current I <10mA/cm²) and b) at high current I >40mA/cm² and c) Cu surface morphology (d inset image of c)

On the SEM imaging, we observe that the Cu layer is denser on the **Figure 4.a** due to the low current injected during the electrochemical deposition. While on the **Figure 4.b**, the layer has a dendritic shape that presents a poor density. Although it has good electrical conduction it remains mechanically friable. The surface morphology of the layer deposited at low current density (**Figure 4.b**) shows a cauliflower shape that explains its good density.

The homogeneous deposition of Cu on the laser opened grid is also critical. The 1mm large busbar receives less Cu than the finger which is only 150µm wide due to the same current density applied in electrochemical process. Thus the fulfilling of the busbar results sometimes in a rupture of continuity of the deposited metal. A deposition in a two steps avoids this discontinuity. Electrochemical deposition begins with a low current density in the first 15 seconds and then it is increased to get several microns of deposit.

2.4 EDS Line scan analysis of Ni/Cu deposit (before and after annealing)

The analyzed area on the sample before annealing is shown in **Figure 5.a**. EDS linescan giviES the qualitative composition of the different regions and the blue arrow indicates the position and direction of the line scan.The EDS analysis shows the presence of Cu deposit before annealing. However, after annealing the spectrum shows the disappearance of Cu.

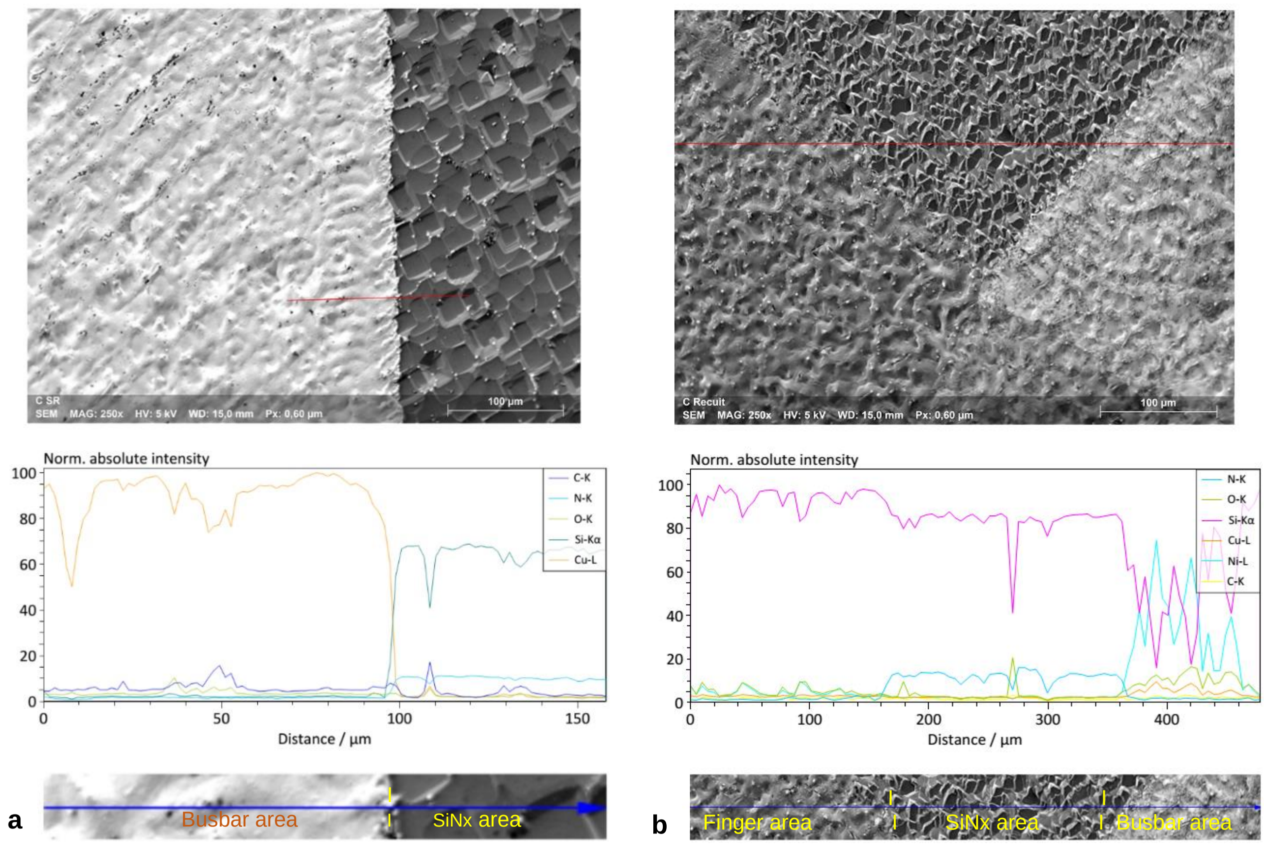

Figure 5 Image and spectra EDS-linescan of the analyzed busbar – SiNx and Finger area a) before and b) after annealing (the scan corresponds to blue line)

In the linescan analysis of Cu/Ni deposit without annealing (**Figure 5.a**), the analyzed area is the region comprising a busbar (0-100µm) and a SiNx zone (100-160µm). The line travels 160 µm from left to right of the busbar towards the SiNx. The elements analyzed are Cu, Si, N, O and C. The linescan spectrum clearly identifies the 2 zones: the busbar and the SiNx layer. In the busbar zone, Cu appears in very large quantities with 95% of the signal. C and O are present in very small quantities. The Cu is therefore deposited uniformly on the busbar. Note that Ni does not appear in this spectrum because it is located under the Cu which covers it entirely. On the SiNx layer, the Cu disappears and the Si and N appear with signals of 70% and 10% with residual C.

The linescan spectrum of Cu/Ni deposit with annealing (**Figure 5.b**), reveals the area comprising a finger (0-160µm) a zone of SiNx (160-365µm) and a busbar with Cu/Ni (365 -480µm). The line travels 480 µm from left to right and reveals the elements Si, N, Cu and O. Si and N elements are related directly to the SiNx layer and O is related to Cu and Ni oxidation. The Si in purple is present in large quantities on the SiNx. The Si is also found on the finger, which denotes that the Cu has disappeared on the finger. The SiNx zone is clearly identified between 160µm and 370µm where we only find N linked to Si.

On the busbar we clearly identify Ni and also Cu in smaller quantities, 7 times less intense than Ni. Annealing greatly reduced the Cu. Oxygen is present in greater quantities (twice more) than Cu. This implies that the Cu was oxidized after annealing.

Annealing caused both oxidation and exo-diffusion of Cu. Annealing also made it possible to reveal the underlying Ni which was obscured by the Cu before annealing.

In conclusion and in order to avoid the loss of Cu by exo-diffusion, it is necessary to carry out the annealing of the Ni just before the deposition of the Cu. Even the oxidation of Cu will be lower.

2.5 Pinhole on SiNx layer

The SiNx layer must not be porous to avoid Ni and/or Cu deposition. This creates pinhole that will be a hotpoint on the surface as shown in **S**4 point of **Figure 6.** We find Cu and Ni at 5.30% and 3.37% atomic. To avoid pinhole creation, SiNx layer have to be deposited at low energy Plasma Enhanced Chemical Vapor Deposition.

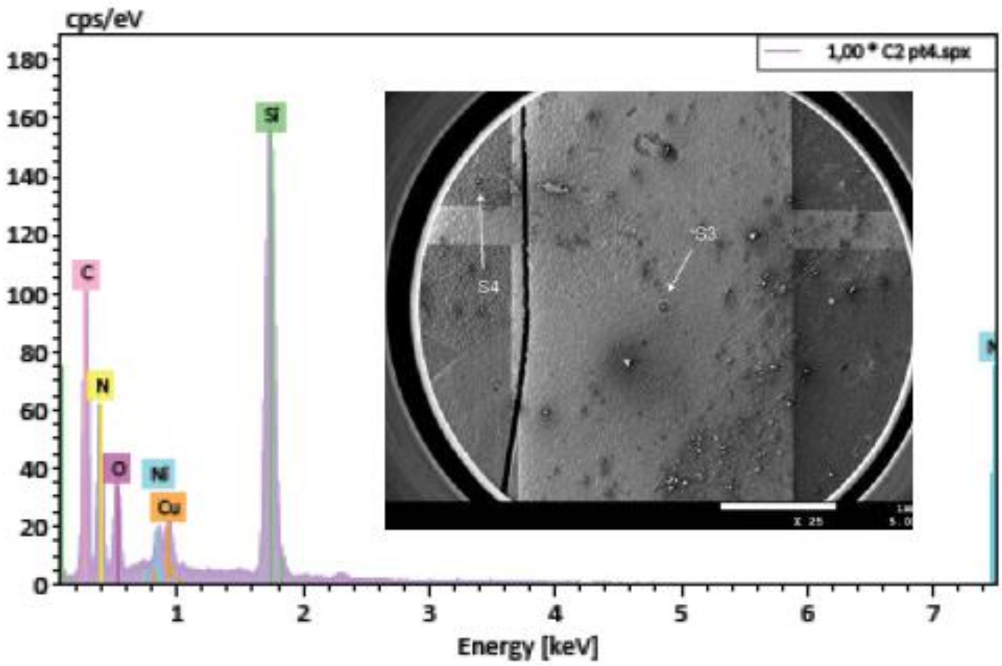

Figure 6 EDS analysis of a pinhole on PECVD SiNx layer.

2.6 Electrical measurement

The Cu layer deposited at low current density shows a shunt resistance measured with suns Voc technique of 264 Ω.cm^2 while in high current density Rsh drops to 19.73 Ω.cm^2 that is more than 13 times better. Moreover the series resistance is similar for both deposits. Indeed the dendritic shape allows a good electrical conductivity even though it has a bad adhesion on Si. In the same time the open circuit voltage Voc is of the same order around 567mV.

3. CONCLUSION

This study has shown some drawbacks of the Cu contact deposition on silicon solar cells. The conditions of a good contact deposition are tightly related to the surface preparation. The problem of adhesion and the quality of the deposited film are presented, discussed and solutions are presented. The key element is the SiNx ablation by laser. The speed and power must be selected to ablate the SiNx layer without letting a residual trace of SiNx. For Ni adhesion enhancement, annealing is made under inert atmosphere and followed by slow cool down.

The density of the Cu layer is better when deposited at low current density.

ACKNOWLEDGEMENTS

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