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Crystalline Silicon Solar Cells with Nickel/Copper Contacts

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1. Introduction

In silicon solar cell technology, metallization plays an integral part in outlining the cost and efficiency of solar cells. Indeed, the development of better techniques for the metallization of silicon solar cells is vital for achieving higher efficiencies. Presently, screen-printed contacts are primarily employed in photovoltaic industry as they can be realized easily with high throughputs. However, screen-printing technology has the draw-backs of higher contact resistance and lower aspect ratios, degrading the solar cells' performance. In recent years, an overall decrease in the photovoltaic module price index has occurred, while the higher cost of silver has disturbed this decrease adversely [1]. The future of solar cell technology will involve decreasing the wafer's thickness as well as decreasing the use of silver according to the standards set out by the international technology roadmap for photovoltaics (ITRPV) [2]. Metal contacts with superior electrical performance and lower production costs are vital for photovoltaic industrial production. In short, the pressing process of screen printing technology for thinner silicon wafers, along with expensive silver pastes, needs to be replaced by a fresh metallization technology. A series of workshops have been dedicated to the metallization of crystalline silicon solar cells, where various metallization techniques have already been inquired [3-6]. All of these meetings have helped in understanding and reforming present-day advancements in solar cell metallization techniques.

Among the capable metallization techniques, contacts composed of nickel/copper (Ni/Cu) metal stacks are considered to be one of the most feasible candidates for future metallization technologies. The use of such metal stacks offers precise and low contact resistance and also helps in improving solar cells' efficiency [7]. The most important feature is that the technique can be realized with lower material costs. Ni/Cu contact formations involve two major steps: a Ni seed layer formation followed by a Cu metal deposition as a front electrode. The Cu metal stack over the Ni layer plays the role of the main contact to the front of the cell [7-12]. The Cu

front metals stack is usually formed by an electro-plating process, which is a well-developed plating technique and can only be applied to conductors. Cu has also been deposited by an electroless plating process, but it also requires a seed layer at the silicon surface [13, 14]. An auto-catalytic method of depositing Ni-phosphorus or Ni-boron by electroless plating bath compositions can be adopted to contact the semiconducting surface of silicon [15-17]. The use of a seed layer (i.e., Ni) can help to plate metal stacks on semiconducting or even non-conducting materials. Apart from Ni deposition from a conventional Ni plating bath, it can be plated under illumination (light-induced electroless plating) [18, 19] or by laser-assisted electroless plating [20]. A galvanic deposition method was also adopted to realize thin Ni layers on a textured silicon surface uniformly [21]. The Cu metal is usually electroplated by a light-induced plating (LIP) process developed at the Fraunhofer Institute for Solar Energy (ISE) [22, 23]. The LIP process involves the immersion of a sample composed of an np-junction with aluminium (Al) screen-printed on the back into an illuminated plating bath. The details of the LIP process will be discussed in the following sections.

This chapter deals with issues regarding contact formations using Ni/Cu metal stacks for crystalline silicon solar cells. The key issues for the discussed technology are: (i) an effective Ni seed layer formation, and (ii) the development of Cu metal contacts by the LIP process. In this section, we will give an overview of the process conditions for such metallization schemes and of the current research work as well as the challenges and issues that have emerged. The sections are dedicated to addressing the most important topics in detail.

2. Silver *vs.* copper metallization

Currently, the photovoltaic industry is primarily occupied by metallization schemes composed of silver-based (Ag-based) screen-printed contacts. The key attribution is a simple process control with an attainable mass production on the industrial scale. However, the efficiencies of cells with screen-printed electrodes are degraded by factors such as the finger width and fill-factor (FF). Ag-based screen-printed contacts usually offer high contact resistance and have lower metal conductivity, and junction shunting can occur during the contact firing process. Such issues degrade the FF of the cell, which is why screen-printed contacts typically offer FFs within the range of 75-78%. On the other hand, the FFs of the contacts patterned with the photolithography process lies within the range of 81-82% [24, 25]. Moreover, screen-printed contacts offer higher shading losses because of larger finger widths (usually $\geq 100 \mu\text{m}$ wide).

The metallization of solar cell has a vital role in contributed to cell performance and it also determines a considerable number of cell processing costs. On average, about 40% of expenses are associated with the pastes used for front-and rear-side metallization [1]. This shows that the overall cost of the solar modules can be reduced drastically if the expensive Ag paste is replaced by relatively cheaper materials, such as copper. The schematics of both the metallization concepts are shown in Figure 1.

Considering the higher cost of Ag and tarnished cell parameters due to shading losses and lower FFs, screen-printed contacts offer an opportunity for replacement by an alternate metallization. Recently, metal contacts composed of Ni/Cu metal stacks have emerged and are

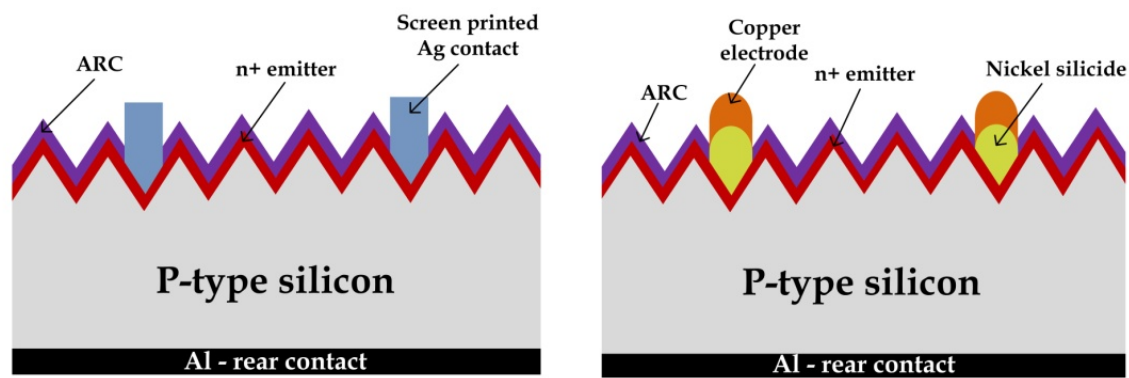


Figure 1. Schematic structures of solar cells composed of metal contacts formed with screen-printed Ag paste (left) and Ni/Cu plating (right).

considered to be a potential candidate for future crystalline silicon photovoltaic cells. Ni/Cu has shown some good results for solar cell performance in terms of improved FFs and higher efficiencies. The overall cost per watt-peak (W_p) can also be decreased as the copper is cheaper than Ag (about 100 times) and is almost equally conductive [26, 27]. It has been reported that Ni/Cu-in comparison to Ag paste-has higher electrical conductivity and lower contact resistance, even at lower doping concentrations (N_s) [28]. Cu is usually deposited by a self-aligned electro-plating process which helps to plate electrodes with finer line widths. The electrodes are plated and processed at lower temperatures (250-450 °C), considerably lower than the temperatures (700-850 °C) required for Ag pastes. The low temperature process is favourable for cell processing, as the degradation of the passivation layers can occur at higher temperatures. Furthermore, the rear side Al contact may be melted as well if Ag pastes are fired at higher temperatures. Although Cu offers certain advantages, it can create highly active generation/recombination centres if diffused in silicon [29]. In order to prevent Cu diffusion in silicon, a barrier layer is required. It has been reported that Ni plays a vital role in reducing the contact resistance as well acting as an effective diffusion barrier between Cu and silicon [30]. In Table 1, both the metallization schemes are compared in terms of the advantages and issues that they offer to crystalline silicon solar cells.

Contacts	Advantages	Challenges
Ag contacted cells	Simple process control High throughputs	Expensive
		Poor aspect ratios
		High contact resistance Lower cell efficiency
Ni/Cu plated cells	Lower price	Complex process Back-ground plating Poor adhesion to Si
	Lower shading losses	
	High aspect ratios	
	Low contact resistance Higher efficiency potential	

Table 1. Comparison of the solar cells fabricated with screen-printed Ag contacts and Ni/Cu metallized solar cells.

3. Ni/Cu contacting schemes

Cu metallization offers greater resistance against electron migration and has been implemented widely for ultra-large-scale integrated circuits (ULSIs). However, it has a major weakness as being a deep-level impurity in silicon and can disturb the electrical performance of the device. These impurities tend to generate traps which act as generation/recombination centres and degrade the minority carrier lifetimes in the substrates [31, 32]. To avoid the Cu from being diffused in the silicon, Ni, as a diffusion barrier, has been employed successfully. Ni not only acts as a diffusion barrier but also promotes adhesion between Cu and silicon [9, 33]. Cu along with a Ni seed layer has given some promising results in terms of the efficiency of the crystalline silicon solar cells. The metallization technique using Ni/Cu metal stacks mainly involves two steps:

- i. Ni seed layer deposition.
- ii. Cu deposition by LIP.

The two step process (seed and plate) for the metallization of solar cells increases the efficiency potential considerably [34]. After depositing Ni/Cu metal stacks, a thin capping layer of silver (Ag) or tin (Sn) is usually electroplated above the Cu. The purpose of this capping layer is to prevent the Cu metal lines from being oxidized. Moreover, these capping layers help to solder the interconnecting tabs and also prevent the Cu interacting with the EVA encapsulant. The processing steps involved in metalizing the Ni/Cu/Ag or Sn metal stacks are shown in Fig. 2. However, the schematics for these steps are shown in Fig. 3.

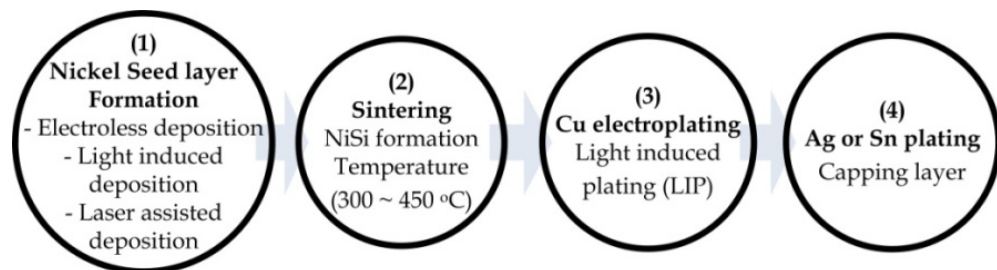


Figure 2. Processing steps involved for depositing Ni/Cu/Ag or Sn metal stacks.

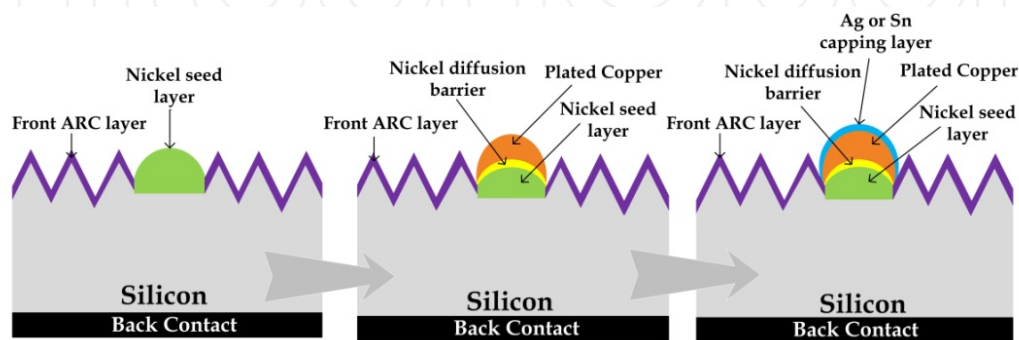


Figure 3. Schematic structures of the steps involved in the formation of Ni/Cu/Ag or Sn-based metallization schemes.

3.1. Ni seed layer deposition

Ni as a seed layer has to be deposited to prevent the diffusion of the Cu in the silicon. There are a number of ways to effect Ni deposition by adopting the mechanism of oxidation reduction reactions. The diffusion barriers used as alternatives to Ni include titanium (Ti) and tungsten (W) [35]. However, Ni has the ability to provide a lower contact resistance to doped silicon and it works well as a diffusion barrier [28, 36]. Low resistivity ohmic contacts can be made by initiating a low temperature sintering process after Ni deposition [8, 11, 36-38]. The basic requirement of the Ni seeding layer formation is a uniform and adequate thickness over the entire front grid. The effectiveness of the Ni barrier layer can be defined by its role in blocking Cu diffusion. In this section, various methods adopted to form a Ni diffusion barrier at various research institutes will be discussed.

3.1.1. Electroless deposition

This type of process is done without the application of any external power source. The process involves autocatalytic chemical reduction reactions to deposit metal layers. The electroless plating deposition principle is shown in Fig.4, where the reduction of metal cations occurs by electrons produced from a reducing agent. The actual electrochemical nature of the process written for the z-valent metal in the form of two half reactions is also shown in Fig. 4 [39]. The final product of the reactions comes in the form of metal deposition on the substrates. The most important feature of the electroless deposition process is that it is capable of metalizing semiconducting or even non-conducting surfaces, such as plastics, ceramics and glass.

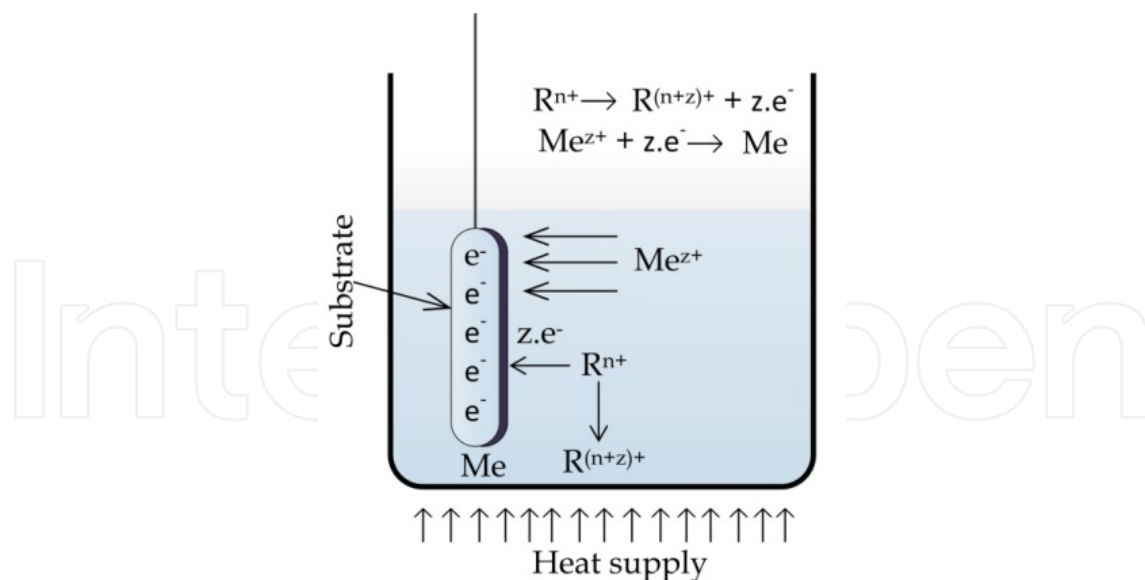


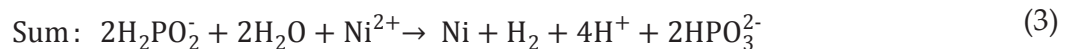
Figure 4. Electroless plating deposition principle for: the oxidation of the reductant and metal layer formation from the reduction of metal ions [39].

The Ni electroless plating bath is composed of the following bath compositions [40]:

- A source of nickel from nickel sulphate ($NiSO_4 \cdot 6H_2O$) or nickel chloride, ($NiCl_2 \cdot 6H_2O$).

- A reducing agent of sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$).
- A buffer or mild complex agent of triammonium citrate $[(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7]$.

Additionally, a small amount of ammonium hydroxide (NH_4OH) is also added to elevate the pH of the solution. The pH of the plating bath should be maintained at around 8 ~ 10 for bath stability and uniform deposition rates [10, 16, 41]. The chemical reactions based on catalytic oxidation-reduction between hypophosphite ions and Ni can be described as the sum of two simultaneous steps [27]:



3.1.2. Light-induced deposition

Light source along with an electroless deposition process were used to deposit a Ni barrier layer. The phenomenon of a chemical reaction taking place is the same (catalytic oxidation-reduction) as described in the previous section. However, the light source provided here helps in adjusting the electrochemical potential of the front and rear of the cell and enhances the plating rates [42]. The electron migration at the surface is controlled by the photo-voltage generated from the np-junction and the electronegativity of the substrates. Moreover, higher plating rates can be achieved as these photo-generated electrons enhance the reduction of the Ni^{2+} ions on the silicon surface [15]. The increase in the plating rates due to light inclusion relieves in the form of operating the bath at lower temperatures. Although a uniform Ni layer at higher plating rates can be deposited, the process of light-induced electroless plating involves complexity related to the process's characterization. Furthermore, the light-induced current in the LIP process helps to transport electrons only to the n-type surface, which limits the technique in metallizing n-type surfaces [43]. The light-induced nickel plating (LINP) process was also investigated by Yu-Han et al., and uniform Ni surfaces of high intrinsic quality were reported [44].

3.1.3. Laser-assisted deposition

Laser-assisted deposition has also been used to employ the Ni deposition process on a silicon surface. The process is considered to be feasible for industrial applications, as the anti-reflection coating (ARC) layer can be ablated along with the Ni deposition. This can reduce the number of steps involved in cell processing and can help the development of solar cells with mass production on the industrial scale.

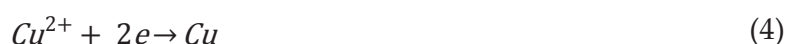
Here, an electrolyte solution is used where a cell composed of an np-junction is immersed and a laser beam is applied to pattern the grid at the wafer surface. The application of the laser beam increases the temperature in the solution and at the wafer surface [20]. The ARC is ablated due to the heat generated at the laser-exposed surface and increased temperatures in the electrolyte solution decompose the Ni particles. Furthermore, the light induced in the cell generates an electron-hole pair, the generated electrons support Ni deposition at the sample surface. The use of water containing Ni salts is considered to be useful for depositing the Ni layer on the silicon surface uniformly. There has been some progress reported regarding laser chemical Ni deposition by various research institutes [45-50], although the process still needs to matured. Laser chemical metal deposition (LCMD) is a solution for implementation on the industrial scale since ARC ablation along with Ni deposition can be performed at the same time. The LCMD process was successfully implemented at Fraunhofer ISE to form Ni-based Cu metallization with 17.9% efficient cells on CZ substrates [51]. Röder et al. also reported a laser-based method to deposit a Ni layer with thinner finger widths ($< 30 \mu\text{m}$) with a low temperature process known as 'laser transfer contact' (LTC) [52].

3.2. Nickel sintering

In order to form a contact between the deposited Ni and silicon, a sintering step is required to form Ni silicide [38, 53, 54]. This sintering process helps to form an alloy of Ni and silicon and it act as a seed layer for the Cu. Furthermore, the sintering process reduces the contact resistance between the metals and the silicon interface [33]. The process involves heat treatment in the ambience of N_2 gas, and Ni is known to form various phases at different temperatures [55]. Three different phases of Ni_2Si ($\sim 300^\circ\text{C}$), NiSi ($300\sim 700^\circ\text{C}$) and NiSi_2 ($\sim 700^\circ\text{C}$) can be realized after the sintering process. The NiSi phase offers the lowest resistivity ($\sim 14 \mu\Omega\cdot\text{cm}^2$) among all three phases and is suitable for solar cell applications [10].

3.3. Copper electroplating

Subsequent to the Ni seed layer's formation with the sintering process, the deposition of a suitable metal is required in order to further reduce the line resistance of the front grid. Materials such as Ag and Cu have been deposited by using electroplating arrangements. Cu is under consideration, since it is relatively cheap in comparison to Ag and it can reduce the overall cell costs drastically. To deposit Cu, an electrolytic metal deposition method can be used. Here, a sample composed of a np-junction and a Cu anode is immersed into an admixed solution of copper sulphate ($\text{CuSO}_4[\text{H}_2\text{O}]_5$) and sulphuric acid (H_2SO_4) [56]. The $\text{CuSO}_4[\text{H}_2\text{O}]_5$ supplies, the Cu (positively charged) and SO_4 (negatively charged) ions for the electroplating process. A positive potential is applied at the anode while the sample is kept at the negative terminal. This applied potential attracts the positively charged Cu ions towards the cathode and the negatively charged SO_4 ions towards the anode. According to the reactions shown in Eq. 4, the Cu deposition occurs at the cathode due to the reduction of Cu ions [39].



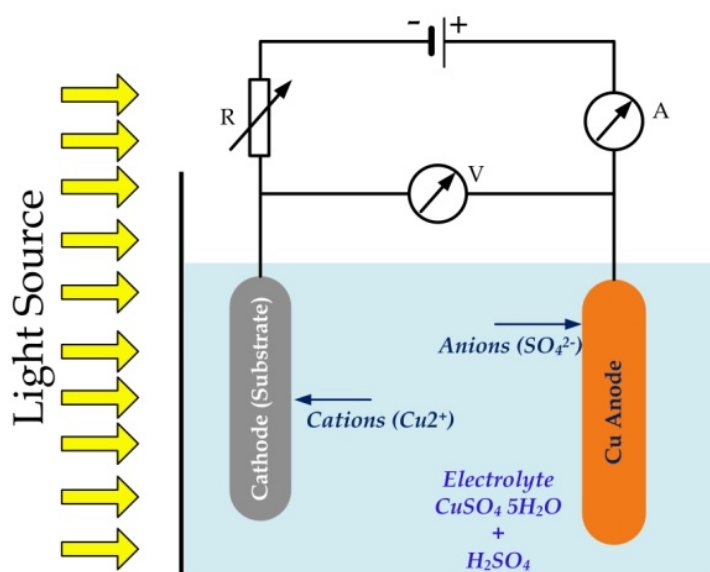


Figure 5. Schematic arrangements of Cu-based light-induced electroplating systems.

The Cu electroplating is mostly done by the approach implementing LIP arrangements as shown in Fig. 5. The LIP process works on the same principle as the conventional electroplating process; however, the inclusion of a light source enables the utilization of the photo-generation property of the solar cell. This process, developed at Fraunhofer ISE, includes the immersion of a patterned cell into the electrolyte plating with the light source arrangements. A protective potential is applied at the sample in order to make the rear-side of the cell more cathodic, which helps in minimizing the corrosion of the aluminium back-electrode. Furthermore, the plating can also be done relatively uniformly, as this potential operates the cell closer to its short-circuit conditions [43]. As to having a uniform voltage distribution across the grid pattern, the LIP process also provides stable baths with no reducing agents. LIP is an encouraging method, particularly for the solar cell metallization since it helps to deposit metal with higher aspect ratios and higher deposition rates.

3.4. Anti-reflection coating (ARC) patterning

The conventional Ag metal contacts are usually formed by screen-printing and firing the Ag pastes through SiN_x passivation layers. However, Ni/Cu-based metallization requires a separate step to open the ARC/passivation layer in order to form the contact grid. A simple example could be a mask and etch sequence [42]. Under this method, the passivated front surface of the cell is patterned with a photolithography process and the unprotected passivated layer is etched away using wet etching. Later on, the photoresist (PR) material is stripped away in an organic solvent solution (the process sequence is described in Fig. 6). For patterning the front contact grids, various approaches have been adopted. These approaches can be categorized as wet etching, direct etching, mechanical scribing and laser-assisted etching. All these etching methods will be discussed in this section of the chapter.

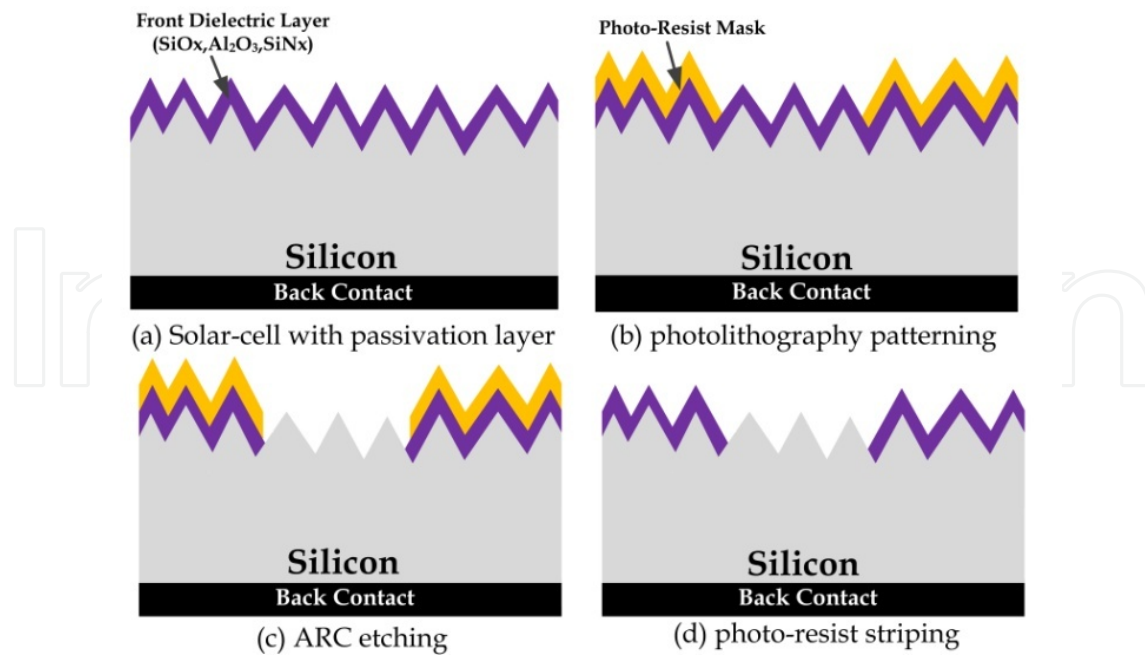


Figure 6. Mask and etch process sequence: (a) solar cell with a passivation layer, (b) front-electrode patterning with a photolithography process, (c) exposed ARC etching, and (d) PR removal.

3.4.1. Wet etching

The process of wet etching involves the front-electrode grid opening in the passivation layers through a wet chemical solution (e.g., hydrofluoric acid). An example of a mask and etch sequence using a photolithography process has already been discussed. The photolithography process has the ability to open finger lines with lower widths (reduced shading losses). Although the photolithography-based grid patterning has shown great results in the form of higher efficiencies, nonetheless the process complexity limits its implementation on the industrial scale. Other methods, such as the use of etch resists deposited by either screen printing or ink-jet printing followed by ARC etching by wet chemical treatment, have also been employed [57, 58]. The ink-jet by aerosol jet printing has also been used to etch away the contact grids by non-contact writing for front metallization [23, 57]. The wet etching methods involve some cleaning steps, which restrict their implementation on the industrial scale.

3.4.2. Direct etching

The application of appropriate etching pastes can also be helpful in etching away the passivation layer directly [59-61]. The process is done by applying phosphoric acid-based etch pastes on the ARC layer followed by temperature curing (at 300-390 °C) to etch away the desired passivation layer. Thinner finger lines (85 μm wide) have been realized by screen printing a phosphoric acid paste and curing at 350 °C for 90 seconds on a textured surface [58]. Another form of the direct etching of the passivation layer was reported which uses a water-soluble acidic polymer with a fluoride-based solution for the etching of SiN_x and SiO_x layers [62]. The method uses the fluoride-based solution-it is safer to handle in comparison to HF-

based etching solutions. Furthermore, lower expenses are involved and the method produces less waste.

3.4.3. *Laser ablation*

Laser-based front-contact openings and metal deposition are considered to constitute the most appropriate method for fabricating cells with Ni/Cu contacts on the industrial scale. In 1990, laser-based contact patterning was done for EFG polycrystalline silicon solar cells [63]. The laser process was used to fabricate laser-grooved buried contact (LGBC) solar cells at the University of New South Wales (UNSW), Australia [64]. Later on, a BP Solar was involved to produce LGBC solar modules commercially [65].

Laser-based ARC ablation can not only help in patterning the grid more easily with Ni deposition, but can also assist in producing cells with higher efficiencies. Thin-width laser grooves for the LGBC cells and selective emitter doping can be performed with the laser-based process for solar cell applications. Thinner finger lines and selective emitter doping ensure that a high open-circuit voltage (V_{oc}) and higher efficiencies can be realized. Moreover, the heavy diffusion step for selective emitter solar cells can be conducted relatively easily [66, 67]. At Fraunhofer ISE, laser chemical processing (LCP) was demonstrated involving the performance of local etching by the use of phosphorus doping and laser grooving with damage free silicon microstructuring [68]. LCMD and LTC methods were also adopted to pattern the front-contact grid and Ni seed layer deposition simultaneously for solar cell applications [51, 52].

3.4.4. *Mechanical scribing*

The front and rear contacts of the solar cells can be patterned by a process called ‘mechanical scribing’. Here, an artificial diamond tip is used to scribe a uniform and shallow depth over a given surface area. The method has the advantage of process simplicity and it can be helpful in patterning the solar cell surface with high throughputs. A mechanical scribing method was used to make grooves for buried contact solar cells [69]. Passivated emitter rear-cell (PERC) solar cells with a back-contact formed by a mechanical scribing process were also reported [11]. Solar cell efficiencies of more than 20% were achieved for such PERC solar cells. An artificial diamond tip of about 10 μm was used to pattern SiO_x and SiN_x passivation layers, while Si-enriched SiN_x layers were found to be etched away easily. Solarex Corporation, USA, used a diamond blade to form deep grooves with widths within the range of 25–45 μm for solar cell applications [70]. Mechanical V-texturing for buried contact solar cells on multi-crystalline silicon with a record 17.5% efficiency was also reported [71].

4. Potential and commercial aspects

Copper can be the best alternative to silver in the front-electrode formation of crystalline silicon solar cells. The main motivation derives from the fact that it exhibits conductivity almost equal to silver, while its cost is about 100 times lower. The higher efficiency potential of the copper in terms of lower shading losses and higher FFs also provides additional benefits compared

to its counterparts. However, the commercialization of Cu-plated contacts is limited at present. In this portion of the chapter, the potential of Cu plating for crystalline solar cells will be discussed. State-of-the-art research developments in the field of crystalline silicon solar cells composed of Ni/Cu-plated contacts will be addressed.

4.1. High efficiency potential with n-type substrates

In recent years, the growth and increase in efficiency of silicon solar cells have been observed. N-type silicon substrates have emerged as a potential material offering considerable advantages for high efficiency photovoltaic module production on the industrial scale [72]. Based upon n-type silicon substrates, SunPower and Panasonic have already presented 24.4% IBC [73] and 24.7% HIT [74] solar cells, respectively.

Ni is known to form ohmic contacts to both p-and n-type silicon surfaces [75]. However, Ni/Cu metallization schemes for n-type substrates can play an important role in cost reduction and the improvement in the efficiency of cells (improved FF, less shadowing). It has been observed that a base material of n-type against p-type silicon has improved stability in relation to thermal Ni contact formation [76]. For a boron-doped p⁺emitter on n-type silicon substrates, contact resistivity of up to 0.6 mΩcm² has been achieved [77]. An efficiency of 20.5% with a FF of 79.2% has already been achieved for a n-type rear-junction cell composed of Ni/Cu/Ag metal contacts [78].

4.2. Current industrial trends

Additional steps for front-contact patterning and Ni seed layer formation with a sintering step followed by Cu electroplating makes the process more complex for Ni/Cu metallized silicon solar cells. At present, Ni/Cu contacts have seen limited implementation on the industrial scale. Modules based on laser-grooved buried grid (LDBG) cells from BP Solar were only produced commercially [79]. However, there has been a lot of progress in terms of increases in solar cell efficiencies. More than 20% efficiencies have already been achieved at Fraunhofer ISE, Interuniversity Microelectronics Centre (IMEC), Kaneka, Roth & Rau Research and Schott Solar [78, 80-83]. Many research institutes have been involved in investigating metallization schemes composed of Ni/Cu metal stacks [8, 10, 13, 42, 84-90].

Thus far, efficiencies of up to 23.5% for a Cu-plated heterojunction-type solar cell have been achieved by Kaneka [80]. Roth & Rau Research also came up with a 22.3% efficient heterojunction cell with Ni/Cu contacts [81]. For a passivated emitter rear cell (PERC), solar cell structure efficiencies above 20% have already been demonstrated by Fraunhofer ISE, Schott Solar and IMEC. Fraunhofer ISE and Schott Solar presented efficiencies of 21.4% [82] and 21.3% [91], respectively. However, at IMEC, an industrially applicable Ni/Cu-plated i-PERC-type solar cell with an average efficiency of 20.5% (more than 100 cells) and a best cell efficiency of 20.79% has been fabricated [83]. IMEC also investigated the application of Ni/Cu contacts for a rear-junction solar cell on a n-type substrate and achieved a best cell efficiency of 20.5% [78]. Ni/Cu metal stacks were also applied to contact laser-doped selective emitter (LDSE) solar cells. LDSE-type solar cells with efficiencies of 19.8% and 19.64% were developed at Hyundai

Heavy Industries and Shinsung Solar, respectively [86, 92]. A 19.33% efficient LDSE-type solar cell with Ni/Cu contacts was presented at the UNSW [93]. More recently, a laser-doped Cu-plated bifacial silicon solar cell exceeding 19% efficiency was developed at UNSW [94]. Solar cells consisting of Cu-plated contacts and exceeding 20% efficiency are presented in Table 2.

Research Centre	Type	V_{oc} (mV)	J_{sc} (mA/cm ²)	Fill Factor (%)	Efficiency (%)	References
Kaneka	Hetero-junction	737	39.97	79.77	23.5	[80]
Roth & Rau	Hetero-junction	734	38.1	79.9	22.3	[81]
Fraunhofer ISE	PERC	679	38.8	81.5	21.4	[82]
Schott Solar	PERC	665	39.9	80.5	21.3	[91]
IMEC	PERC	649.8	39.3	78.3	20.79	[83]
IMEC	Rear Junction	676	38.4	79.2	20.5	[78]
Fraunhofer ISE	-	646.4	38.86	80.8	20.3	[42]

Table 2. Solar cells consisting of Cu-plated contacts exceeding 20% efficiency.

5. Challenges and open research issues

Higher efficiencies for Ni/Cu contacts have been achieved, with a reported cell efficiency as high as 23.5% for a heterojunction solar cell on CZ wafers [80]. The potential high efficiency and lower processing costs of Ni/Cu-based metallization compared to its screen printing counterpart is striking; however, there are certain factors that limit its implementation on the industrial scale. It is assumed that replacing Ag-based metallization by Ni/Cu contacts could reduce the overall cost, yet the cost of ownership for Ni/Cu contacts needs to be reviewed. If it only concerns material costs, Ni/Cu may be beneficial. However, the additional process complexity and the replacement of an Ag screen printer/dryer with equipment comprising a laser, plating arrangements and a sintering furnace should be kept in mind. Apart from the issue of process complexity, in addition contact adhesion, background plating and-more importantly – long-term reliability need to be addressed.

5.1. Process complexity

To realize Ni/Cu metal contact for solar cell applications, a number of processing steps are required. Steps such as ARC opening, Ni deposition/sintering and Cu electroplating are required. These steps make the process more complex and difficult to implement in mass production. To realize such a metallization scheme on the industrial scale, the processing steps need to be minimized. The use of lasers for depositing a Ni seed layer could help to decrease

these processing steps to some extent by combining ARC ablation and the Ni deposition process [45]. The conventional electroless plating techniques might be replaced with light-assisted electroless plating for faster and uniform plating. At IMEC, a simple copper metallization process with higher cell efficiencies and a reliable module was presented [95].

5.2. Contact adhesion

Cu exhibits poor adhesion to silicon and requires a seed layer to form an effective and adhesive metal contact. However, Ni has shown some promising results in providing ohmic contact with good adherence to silicon. Further improvements are required to satisfy the standard heat-quenching and peel force tests. Bath-ageing, acidity and residues on the substrate surface have been found to affect contact adhesion adversely [96, 97]. Various research institutes are currently working to improve the adhesion between Cu and silicon in order to resolve this issue completely. So far, IMEC has presented Ni/Cu metals stacks with adhesions within the range of 1~2.7 N/mm [89]. A research team at Fraunhofer ISE has also presented a two-stage process for etching the back of unreacted Ni and re-plating it [98]. Adhesion strengths of up to 2.5 N/mm were achieved by adopting just such a two-stage process at Fraunhofer ISE.

5.3. Background plating

Background plating-also known as 'ghost plating' or 'parasitic plating'-is an unwanted copper plating that occurs at the passivation layers. Inhomogeneities at the SiN_x surface, silicon residuals and cracks are mainly responsible for background plating [99, 100]. The phenomenon may affect cell performance by creating undesirable shading and can divest the solar cell aesthetically. The shading affects cell performance by causing a reduction in the short-circuit current density and can also lead to junction shunting due to metal diffusion [101]. Furthermore, the localized metal silicon contact due to this undesired plating increases the recombination velocity at the surface. The point-like effects and cracks on the samples are the two main types of background plating [99].

An appropriate cleaning step is required before applying the passivation layers to remove forms of silicon residuals. Cleaning in a chemical solution, such as piranha (an admixed solution of H_2O_2 and H_2SO_4) is one way to clean the sample surface properly [99]. Another way to reduce pinholes on the SiN_x surface might be the deposition of thin (10~15 nm) silicon dioxide on diffused silicon before SiN_x deposition [101]. Mechanical stress during the ultrasonic step should be minimized and wafers should be handled carefully to avoid the micro-cracks which cause the undesired metal plating [99, 102].

5.4. Reliability of Ni/Cu contacts

Long-term reliability for Ni/Cu metal stacks is a very important feature and should be considered while evaluating the solar module lifetime. Cu is known to create deep-level impurities if diffused in silicon. Solar cell modules have to fulfil the criteria defined in the form of the IEC 61215 test [103]. The IEC 61215 requirements are to satisfy the conditions of either

1,000 hours damp-heat exposure at 85 °C with 85% relative humidity or a $\leq 5\%$ p_{max} loss after 200 thermal cycles between -40 °C and 85 °C.

Limited progress in terms of reliability for the Ni/Cu contacts has been made, with few reports made so far [81-83]. Fraunhofer ISE and IMEC have tested solar modules according to the criteria defined by the IEC 61215 reliability test. Both Fraunhofer ISE and IMEC have come up with satisfactory results after damp heat exposure and thermal cycling tests [82, 83]. In another report, reliable Ni/Cu contacts for a heterojunction solar cell were presented which successfully passed the damp heat test when conducted for 3,000 hours [81]. In a report from RENA GmbH, Germany, modules comprising Ni/Cu/Sn metal stacks successfully passed the module reliability test, confirming that no Cu diffusion had occurred in the silicon [104].

6. Summary and outlook

A detailed overview of research activities in the field of Ni/Cu-based metallization for crystalline silicon solar cells has been presented. Many research groups across the globe have taken on the challenge of working on crystalline silicon solar cells with Ni/Cu contacts. The Ni/Cu plating, which was the topic of this section, has enormous potential in realizing improved solar cell efficiency and low cell and module costs. The generic built-up process for such metallization starts from the deposition of the Ni seed layer, which offers lower contact resistance when sintered at specific temperatures. A Cu metal is electroplated on top of this stack and after confining this layer by a top Ag or Sn capping layer. The Ni seed layer acts as a potential barrier to block Cu diffusion into the silicon and the capping layer prevents the Cu from being oxidized.

Progress has been made with various deposition options available for Ni in promoting adhesion and a diffusion barrier to the Cu. Electroless chemical baths containing Ni salts and a reducing agent of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ offer a cost-effective deposition process. The inclusion of light source in the electroless plating process results in uniform and faster deposition by utilizing the photovoltaic effect of the solar cell. Various new patterning techniques are available, including the use of etching pastes, aerosol jet and laser-based chemical metal deposition. Laser-assisted chemical metal deposition provides an opportunity to pattern the front contact grid and to deposit the Ni seed layer together. Ni deposition and ARC patterning in a single step is the solution to minimizing the processing steps and reducing the process complexity. It can provide the opportunity for cell production on the industrial scale.

Promising results in the form of solar cells with a higher FF and improved efficiency have been reported recent years. FFs of the range approaching 80% and efficiencies above 20% have already been reached at various research institutes. More recently, at IMEC, an industry-feasible Ni/Cu plating scheme for i-PERC-type solar cells with a best cell efficiency of 20.5% has been presented.

If we consider material cost and cell performance, Cu as an electrode seems to be the best alternative to the existing screen-printed Ag contacts. However, its implementation on the

industrial scale is still limited by a number of obstacles. Recent reports suggest that there has been progress in finding a solution to the hurdles of background plating and adhesion. Surface pre-treatment prior to passivation layer deposition and the low stress handling of the samples yielded an ARC surface with decreased background plating. A uniform Ni seed layer covering the contact area resulted in good adhesion strengths of the Cu lines to n-type and p-type emitters. However, the challenge of finding sustainable and reliable contacts is vital in creating viable Ni/Cu contacts for solar cells on the industrial scale.

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