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Comparison of different electrochemical deposits for contact metallization of silicon solar cells

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ABSTRACT

The aim of the present work is to compare deposits made by electroless nickel–phosphorous (Ni–P) from two different baths and to see how it can be used for the fabrication of solar cell contacts: deposition on screen-printed contacts or directly on silicon as seed layer for subsequent electrolytic deposition of copper or silver. N-type silicon samples were plated, so as to study the feasibility of such deposits (homogeneity, adhesion). Scanning electron microscope (SEM) and contact resistivity measurements by transmission line model (TLM) were used to check the quality of the deposits. Dark *I–V* characteristics and external quantum efficiency have also been performed on standard silicon solar cells before and after Ni–P deposition on screen-printed contacts.

1. Introduction

One of the major problems limiting the efficiency of solar cells is the quality of the contacts [1–6]. Currently, screen-printing is the metallization technique most used in the industry for silicon solar cell production, because it is more cost-effective and that its implementation on a production line is relatively fast and easy to manage. However, screen-printed metal presents high resistivity and porosity and induces wafer curvature after paste annealing especially on thin wafers. Achieving large surface cells on thin substrates while fulfilling the demands of efficiency improvements will require the development of new metallization technologies. The idea is to move towards technologies that are compatible with the industry constraints and do not require photolithography or high temperatures and low pressures and would generate many opportunities, including greater flexibility for passivation layers, reduction of series resistance, improvement of optical confinement and mechanical properties. The electrochemical deposition techniques could be a solution to improve contact [7–8].

The present work focuses on the development of electroless nickel–phosphorous deposition. Indeed, it can be used for deposition on screen-printed contacts in order to facilitate the welding [9] and to improve the conductivity of the contacts or as a seed layer for an electrolytic deposition of copper in order to make contacts directly on silicon.

In this paper, the characteristics of Ni–P deposits from two different types of baths (acidic and alkaline) are presented. Analysis by a scanning electron microscope (SEM) permits to check the quality of the deposits. Then, electroless Ni–P deposition with the acidic bath thanks to a galvanic initiation process was used for deposition on screen-printed contacts. Dark *I–V* curves and external quantum efficiency measurements have been taken before and after deposition in order to see the effect of such deposits on the characteristics of the solar cells.

2. Electroless Ni–P deposition

2.1. Principle

Electroless nickel deposition is an autocatalytic process by immersion of a substrate in a plating bath. It is based on the capture of electrons by the cations present in the solution which are absorbed at the surface of the substrate. These electrons are supplied by a reducing agent dissolved in the solution. In our case, the main electron source is the oxidation of the sodium hypophosphite (NaH_2PO_2). The nickel ions are reduced to solid nickel on top of the silicon. The deposit is not pure nickel but contains phosphorous. The reaction can be summarized as expressed by the following equation [9]:

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni^0 + 2H_2PO_3^- + 2H^+ + H_2 \quad (1)$$

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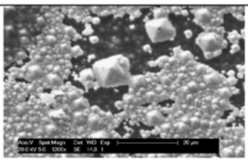
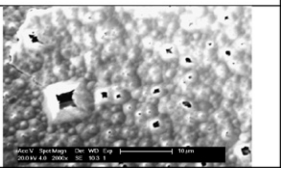
	Deposition time : 1 min Thickness : ~ **0,2 µm**	Deposition time : 2 min Thickness : ~ **0,3 µm**
Substrate after immersion in acidic **Ni-P** bath		

Fig. 1. SEM micrographs and aspect of the Ni–P deposits from the acidic bath.

Two types of baths have been studied: an acidic Ni–P bath (bath1) and an alkaline Ni–P bath (bath2). The characteristics of the deposition for each solution are presented in Table 1.

2.2. Samples preparation

All the preliminary metallization tests have been made by using monocrystalline silicon wafers, p-type, ⟨1 0 0⟩ oriented, 300 µm thick, 1 Ω cm. Si surface has been texturised using a KOH solution: this etching induces pyramidal shaped surface. Samples were submitted to diffusion in $POCl_3$, with an emitter sheet resistance of 40 Ω/□. Samples area is 4 cm^2. Finally, all samples were rinsed for a few seconds in HF solution in order to remove the native oxide on the samples before immersion in the plating baths.

3. Ni–P acidic bath

3.1. Characteristics of the deposits

As no spontaneous plating was observed after immersion in the acid plating bath, a galvanic initiation deposition method was tried [10]. The surface of the samples was activated by contact with a metal which was catalytic in the plating bath, as for example nickel or zinc. The open-circuit potential (also called mixed potential) of the catalytic metal in the plating bath must be able to induce an accumulation of negative charges at the surface of the silicon after contact. This accumulation leads to an increase of the silicon redox potential above the Ni^{2+}/Ni potential. An electron transfer from the semi-conductor to the metallic cations in solution is then possible and the deposition occurs. This allowed the direct metallization on silicon samples by simply touching their surface with the metallic specimen. This process is sometimes called "internal electrolysis". In our case, the contact deposition results from a catalytic mechanism described by the following equations

$$\text{S(non-catalytic)} + {M_1}^{n+} + \text{red} \rightarrow \text{no deposition} \tag{2}$$

$$\text{S(in contact with)}M_2 + {M_1}^{n+} \rightarrow M_1/\text{S} + M_1/M_2 + \text{ox} \tag{3}$$

where S is the substrate to metalize, M_1 is the metal to deposit, M_2 is the catalytic metal, ox is the oxidant and red the reductor.

When one electroless nickel layer is deposited on the surface, the deposition continues because nickel is itself catalytic.

As can be seen in the SEM images in Fig. 1, for a short plating time (1 min), the basis of certain pyramids is not metallized. For longer deposition times, a higher coverage of the surface is achieved. However, the deposit seems non-adherent at the top of the pyramids because it is too thick. Indeed, it has been observed that the deposits are adherent for thickness below about 0.5 µm on silicon.

Table 1
Characteristics of the studied baths.

	Bath1: Ni–P acidic	Bath2: Ni–P alkaline
pH	4.5–5.5	8–10
Temperature	85 °C	90 °C
Agitation	Yes	Yes
Deposition rate	~10 µm/h	~7 µm/h

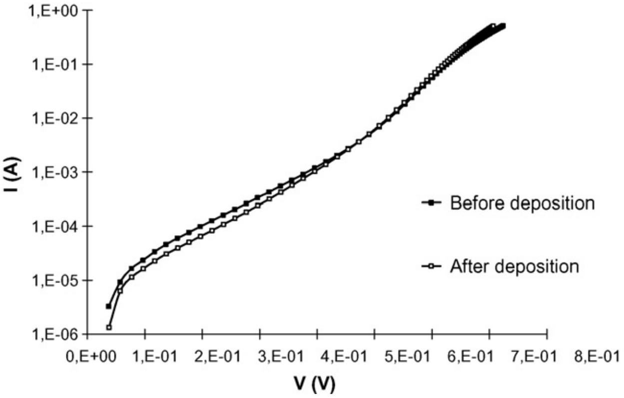


Fig. 2. Typical *I*–*V* characteristic under dark condition of 1 cm^2 solar cell before and after Ni–P deposition.

This problem of surface coverage is due to the activation process. The deposition begins first at the top of the pyramids because they are more in contact with the catalytic metal than the basis of the pyramids. For thick and thin deposits, Ni–P layers are porous and do not constitute a good barrier layer for an electrolytic copper layer. However, no metal deposition was observed on the antireflection coating (*SiNx:H PECVD*) after immersion in baths. Moreover, 1 µm thick metal deposits (and possibly more) are adherent on silver screen-printed contacts.

Despite the fact this bath is not well adapted to metal deposition on silicon, we can conclude that it is suitable for deposition on screen-printed contacts.

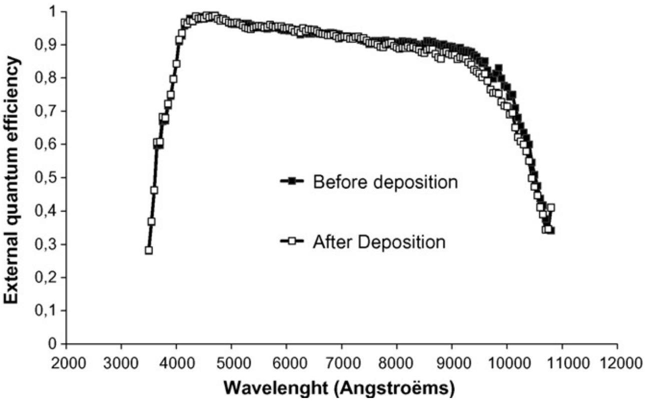


Fig. 3. Typical external quantum efficiency of 1 cm^2 solar cell before and after Ni–P deposition.