



Electroplated contacts and porous silicon for silicon based solar cells applications



Konstantin Kholostov^{a,*}, Luca Serenelli^b, Massimo Izzi^b,
Mario Tucci^b, Marco Balucani^{a,c,1}

^a Department of information engineering, electronics and telecommunications, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Rome, Italy

^b Enea Casaccia Research Centre Rome, via Anguillarese 301, 00123 Rome, Italy

^c Rise Technology S.r.l., Lungomare Paolo Toscanelli 170, 00121 Rome, Italy

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ABSTRACT

In this paper, a two-layer metallization for silicon based solar cells is presented. The metallization consists of thin nickel barrier and thick copper conductive layers, both obtained by electrodeposition technique suitable for phosphorus-doped 70–90 Ω /sq solar cell emitter formed on p-type silicon substrate. To ensure the adhesion between metal contact and emitter a very thin layer of mesoporous silicon is introduced on the emitter surface before metal deposition. This approach allows metal anchoring inside pores and improves silicon–nickel interface uniformity. Optimization of metal contact parameters is achieved varying the anodization and electrodeposition conditions. Characterization of contacts between metal and emitter is carried out by scanning electron microscopy, specific contact resistance and current–voltage measurements. Mechanical strength of nickel–copper contacts is evaluated by the peel test. Adhesion strength of more than 4.5 N/mm and contact resistance of 350 $\mu\Omega$ cm² on 80 Ω /sq emitter are achieved.

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1. Introduction

Silver represents one of the main issues to reduce the silicon solar cell cost per watt. In 2014 the International Technology Roadmap for Photovoltaics (ITRPV) predicts silver reduction down to 50 mg/cell in 2018 [1]. To achieve this goal many researchers are focusing on silver replacement using nickel- and copper-based metallization [2]. This approach introduces several issues to be solved to promote this process at industrial level. It is known that nickel contacts for both n- and p-type silicon exhibit good electrical properties through silicides formation [3]. Nevertheless, nickel alone cannot be used to replace silver due to its conductivity significantly lower than silver. On the other hand copper shows conductivity comparable to silver but copper is a lifetime killer for silicon-based solar cells due to its high mobility inside the silicon crystal even at low temperature [4]. Consequently, a barrier layer is required to prevent copper diffusion and to guarantee low contact resistance on silicon. Two-layer metallization consisting of thin

nickel barrier layer and thick copper conductive layer is a solution to address both metal conductivity and copper diffusion issues.

According to the state-of-the-art, plating is a common technique for nickel- and copper based metallization of solar cells. Today many publications report the application of electroless, electrochemical, or light-induced plating (LIP) techniques, which have been thoroughly reviewed by Lennon et al. [2]. Industrial applicability of the plating processes foresees two main issues. One is the solar cell masking needed to protect the active area of the solar cell, in order to form the front grid metallization. Another issue concerns the cell throughput of plating technique at industrial level, which directly depends on the plating speed. Even though in the semiconductor industry deposition rate of several micrometers per minute is considered rather high, in turn, it does not satisfy industrial requirement of solar cell manufacturing that demands a throughput of more than 1000 cells/h. The most attractive solution is represented by high speed electroplating procedure using localized plating and dynamic liquid drop/meniscus technique, recently proposed in ref. [5,6].

According to the most recent ITRPV overview, before the introduction of alternative metallization technique adhesion issue has to be solved [1]. Adhesion of plated metals to silicon is a well-known issue, indeed special surface treatment is necessary before the metal deposition step [7]. Such surface treatment, as chemical

* Corresponding author.

E-mail address: kholostov@diet.uniroma1.it (K. Kholostov).

¹ Leader of the research group.

etching, results in rougher surface but considering that silicon solar cells are moving to shallower junctions (i.e. 0.3 μm) that roughness can cause damage up to the depletion region. Another approach to the adhesion issue is featuring the silicon substrate with 25 μm deep grooves that allow to anchor metal layers inside the silicon substrate [8]. But now silicon wafers for solar cells are thinner than 200 μm , therefore grooves are not welcomed since they reduce the mechanical strength of the silicon substrate, thus reducing the yield of solar cell production line. On the other hand the use of silicide can promote the adhesion of nickel film plated on silicon [9]. However, recently, it has been shown that poor adhesion of nickel to silicon is still observed even after silicide formation [9]. Accumulation of Kirkendall voids at the silicide–nickel interface, attributed to unbalanced diffusion rates of nickel and silicon into each other and defects inside the plated nickel film can result in poor adhesion on silicon substrate, therefore the uniformity of the silicide–nickel interface becomes relevant, taking also into account that nickel silicide sintering contributes to the contact resistance between metal and silicon emitter layer.

In this work, the electrical contact formation performed by nickel and copper electrodeposition on n-type doped emitter regions of silicon-based solar cells is investigated. The main innovation of this work concerns the introduction of approximately 30 nm thick layer of mesoporous silicon (PS) that allows to simultaneously obtain two characteristics: metal anchoring inside pores to promote the adhesion avoiding emitter damaging and improved distribution of phases due to the large area contact between nickel and silicon for subsequent homogenous silicide formation. Research and application of PS to solar cells lies mainly in the field of antireflection coating (ARC) material and the first development started more than 30 years ago by Prasad et al. [10]. To characterize solar cells having PS as ARC, Vinod [11] studied the application of standard screen printed silver metallization on it. According to his methodology, it was necessary to remove completely the PS layer by molten glass frit contained in the silver paste, to achieve good electrical contact parameters between metal and silicon. Instead, in this work, PS is introduced in solar cell manufacturing process to enhance metal/semiconductor contact performance in terms of contact resistance and adhesion, thus, expecting higher efficiencies for solar cells and better reliability for solar modules. Indeed PS layer having porosity gradient and completely filled with nickel, warranties both electrical and mechanical properties of the metal/silicon contact resulting in adhesion strength higher than 4.5 N/mm and contact resistance of 350 $\mu\Omega\text{cm}^2$ on 80 Ω/sq emitter.

Moreover, cost reduction in solar cell manufacturing can be obtained replacing silver with inexpensive metals (i.e. nickel and copper). To this aim in this work is proposed a very simple technique due to easy and cheap processes, as anodization and electroplating. This technique is not particularly sensitive to sheet resistances and thicknesses of emitters of solar cells, leading to a process easily transferable to the industrial cell manufacturing.

2. Experimental

2.1. Materials

Reagent grade chemicals are used throughout all the experiments. 70, 80 and 90 Ω/sq emitters are formed using POCl_3 diffusion process on pyramid textured mono-crystalline (100) oriented Cz p-type 1 Ωcm silicon wafers. After emitter diffusion, aluminium backside contacts are applied using standard screen printing technique and fired using conventional conveyor belt furnace. These wafers are cut into 2 cm \times 4 cm samples and suitable

structures for contact resistance measurements using Transmission Line Method configuration (TLM) are formed by photolithographic patterns.

2.2. Mesoporous silicon formation

The formation of PS layer on the emitter regions is obtained by anodization in hydrofluoric acid (HF) based electrolytes. Chemical composition of the electrolyte is used starting from 48% HF acid, deionised water and isopropanol mixed in variable ratios. Thicknesses of PS layers around 30 nm are chosen for all the samples. PS layers are formed in both galvanostatic and galvanodynamic regimes using standard two-electrode electrochemical cell. During the anodization, a voltage is applied to the samples to forward bias the p–n junction.

2.3. Metal plating and contact formation

Metal plating of solar cell emitters is performed inside a glass beaker filled with electrolyte. The electrodeposition is obtained using two-electrode configuration. After coating the aluminium backside contact with chemically resistive film, the samples are vertically placed inside the liquid solution. Illumination to promote the plating of samples is then added by Olympus ILK-7B 150 W tungsten–halogen light source. To form nickel and copper layers, Enthone® industrial electrolytes, LECTRO-NIC 10-03 nickel sulfate based and MICROFAB SC 40 MD copper sulfate based are adopted. In order to form high quality dense nickel layers, both plating in galvanostatic regime and the pulse–reverse plating (PRP) technique are studied. The latter process is completely described by Chandrasekar et al. [12]. Nickel plating is carried out onto PS layers and consisted of the two stages. At the first stage, nickel is supposed to fill the pores (i.e. inner volume) of the PS layer. To avoid oxide formation on PS layer that is known to inhibit silicidation process [13], 0.5% fluoride content is introduced into the nickel plating electrolyte. At the second stage, thick barrier layer is formed. Temperature of the liquid solution during plating is kept at 60 °C. Current densities are chosen in the range between 10 and 1000 mA/cm^2 . Thus, around 300 nm thick nickel films are obtained. In order to form the silicide, annealing on a hot-plate for 3 min at 350 °C in air is carried out. Then, 9 μm thick copper layer is deposited on top of the nickel barrier layer, to reduce the overall resistance of the metal contact. Copper layer is formed by electroplating in galvanostatic regime. During the plating procedure, the temperature of the liquid solution and the current density are chosen at 50 °C and 200 mA/cm^2 .

PRP regime consisting of three repeatable steps is used and the current density profile is shown in Fig. 1. At the first step, electrochemical deposition with a short ($t_{\text{dir}} = 100$ ms) pulse of current (j_{dir}) is performed. In order to slightly dissolve the deposit obtained during the first step, the voltage polarity of the electrochemical cell is switched and a short ($t_{\text{rev}} = 100$ ms) pulse of reverse current (j_{rev}) is applied. Then, as third step, a relaxation time of 50 ms (t_{off}) is used to “refresh” the reaction area. Values of these parameters, j_{dir} and j_{rev} , are relevant variables in the investigation. Approximate number of periods of PRP and time of galvanostatic deposition are estimated from the total electric charge value, which is kept in range of 100–300 mC/cm^2 in this study.

2.4. Samples characterization

Carl Zeiss Auriga Cross Beam (FIB–SEM) Workstation is used to investigate surface morphology and composition of samples after anodization and metal plating processes by means of scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX). Samples with PS layers are cleaved along their

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