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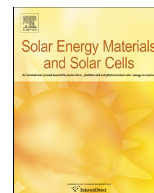

Microstructure analysis of the interface situation and adhesion of thermally formed nickel silicide for plated nickel–copper contacts on silicon solar cells

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ABSTRACT

For low cost high efficiency fully plated NiCu contacts on silicon solar cells, a thermal formation of nickel silicide is commonly performed for adhesion promotion. Since the results of this strategy have been found to be ambiguous, and as the interface situation is not understood, a microstructural analysis of the metal–silicon interface after thermal annealing of plated nickel layers on silicon solar cells has been carried out.

The point of failure upon performing solder and peel testing on sintered contacts has been identified to be at the silicide–nickel interface. Microstructural analysis shows that void formation can be observed at this interface. The mechanisms of silicide and void formation from plated layers on solar cells are studied taking into account different electrolytes and pretreatments. The cavities can be removed by selective nickel etching and replating nickel onto the formed silicide after silicide pretreatment. Excellent adhesion of up to 2.5 N/mm has been measured, which represents the force of silicon wafer breakage rather than true metal adhesive force.

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1. Introduction

Growing economic pressure is increasingly raising the demand for a cost effective metallization of silicon solar cells. In this context fully plated nickel–copper metallization of solar cells features multiple technological advantages compared to standard screen printed silver contacts. Firstly the efficiency potential is higher because of a low contact resistance of silicon to nickel even for lightly doped emitters [1,2] and superior contact geometry with higher conductivity of the very compact metal. Solar cell efficiency has been demonstrated to be comparable to high efficiency TiPdAg metallization technology, which is utilized in space applications [1]. Secondly the utilization of costly metals is omitted in favour of mainly copper, which is available for roughly 1% of the price of silver and can be applied cost efficiently by electrochemical deposition. Therefore a large effort is put into maturation of this metallization technology [2–6]. A concern for cell manufacturers is the detrimental diffusion of copper into silicon [7], which is effectively prevented by the underlying nickel layer for longer than warranty periods [8,9], which are usually greater than 25 years.

The greatest issue for industrial adoption is the generally-found low adhesion of nickel to the silicon surface and this phenomenon is not fully understood. In the past, attempts have been made to roughen the silicon surface chemically [5], or by laser processing [10], which show disadvantages, such as emitter thinning by chemical etching or significant cell degradation by laser impact and may lead to insufficient adhesion for module integration [11]. However, chemical bonds between nickel and silicon can be formed by thermal silicidation. Apart from the undoubtedly positive effects on the contact resistance [12], it appears obvious that such a phase will improve mechanical stability. Consequently, nickel silicide has often been speculated to feature adhesion promoting properties [1,2,8,13,14]. BP solar, who was the first to apply such contacts industrially, states that silicides are responsible for good adhesion [15]. Solar modules featuring NiCu-contacts produced by BP Solar have been in the field for decades without reports of mechanical or electrical failure. These were produced by depositing a thin layer of electroless Ni, thermal silicide formation and additional plating of a 2 μm Ni layer onto the formed silicide followed by electrolytic copper plating. However, the exact process sequence enabling this is not revealed in any of their publications known to the authors. Tjahjono et al. [16] and Russel et al. [17] have shown averaged peel force values of 3.5 N and >2 N for plated NiCu contacts at angles of 180° and 45°, respectively. Kray et al. [11] have published peel force test results for plated NiCu contacts, using the integral peel-off energy

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and stating that adhesion is comparable with screen printed contacts. However, in all of the mentioned studies, there remains at least some uncertainty with respect to the exact process sequence used. Also, there is no clear acceptance in the crystalline silicon PV field about which adhesion test is most appropriate, however it is widely agreed that the 90° peel force test is the toughest examination in this respect. Furthermore, none of the above mentioned studies have addressed the failure mechanism of peel force measurements, i.e. metal peeling or silicon chunks being torn out. No systematic study on adhesion promotion by silicide formation can be found.

In microsystems technology, which is similar to solar technology in several aspects, nickel silicide is also used as contact material for source, drain and gate in CMOS manufacturing [18]. Sputtered or evaporated layers of nickel are converted into silicides in a thermal step, the external connection is then done by vacuum deposition of another metal (mostly tungsten or copper). Most publications in this field are related to specific silicide phase formation control and its relation to contact resistivity, but publications on the topic of adhesion are scarce. This might be related to the facts of technological differences, like surface preparation, vacuum process technology, selective etching of unreacted nickel and possible capping layers and deposition of conductive metals into grooves. PVD deposited layers lead to superior adhesion [19] and grooves inherently feature adhesion promotion.

In this contribution a systematic study of interface situations related to adhesion is presented in the context of plated nickel contacts on silicon solar cells.

2. Experimental

Substrates comprised of Cz silicon wafers with a size of 156 × 156 mm² with a random pyramid texture. They featured a 1.4 μm deep 150 Ω/sq emitter, a 80 nm PECVD SiNx antireflective coating and a full area aluminium screen printed and fired rear side metallization. The ARC was selectively ablated in a grid structure by inkjet-printing a mask and wet chemical etching of the ARC in unmasked areas [20]. A grid design of 10 cells per wafer with a busbar length of 60 mm and a width of 1.5 mm was applied for the Cz wafers, which were designed for peel-force measurements. These small area cells were cut from the wafers using a dicing saw, which simultaneously provides edge isolation.

Prior to plating, any native silicon oxide was removed by a 30 s hydrofluoric acid (HF) dip. Rinsing after HF treatment was performed in an automatic quick dump rinsing tool, which takes roughly 5 min of rinsing time. Nickel deposition was performed in a Ni–LIP laboratory setup following the principle shown in Fig. 1 [1] using Watt's type electrolyte. The electroless plating setup is similar, while no rear side voltage is applied, using a commercial alkaline NaOH based electrolyte with hypophosphate as a reduction agent and a Nickel concentration of about 4 g/l. Electroless Ni with a deposition duration of 90 s was used as a silicidation source and LIP–Ni with a deposition duration of 60 s as a seed layer and Cu barrier in the present work. Similar results using LIP nickel as silicidation source are expected based on similar silicide formation results.

Nickel annealing was performed for 10 min at 450 °C under forming gas atmosphere, to prevent possible oxidation of the Ni layer. These somewhat harsher parameters than typically used for silicidation have been chosen for a clearer view of the microstructural situations by larger structures. This is likely to endanger the cell performance by deep silicide formation, which can lead to current leakage or even shunting of the cell, but these matters are not addressed in this contribution. Other experiments not shown

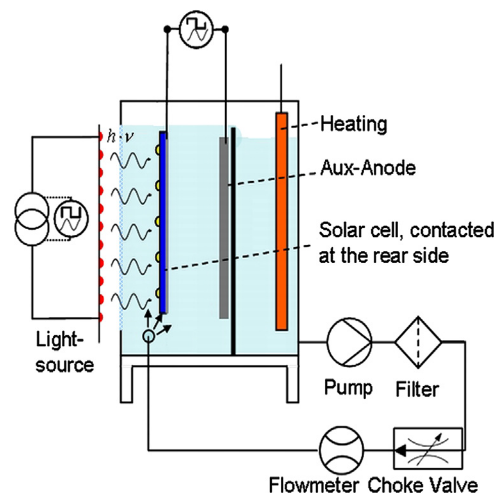

Fig. 1. Schematic light induced plating setup.

in this publication indicate that shorter durations and lower temperatures in the range of 350 °C should be sufficient.

Unreacted nickel was selectively etched by a diluted sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) mixture (SPM), which is standardly used for selective etching of unreacted nickel in CMOS silicide processes [21].

Peel force tests were usually done on a full metallization stack, which consisted of the described nickel seed layer after silicide annealing, a Cu–LIP main layer and an electroless Ag plated capping layer for best solderability.

Cross section preparation was performed by an argon ion beam cutter. Microstructure imaging was performed with a Hitachi TFE-SEM SU-70 with an integrated EDAX EDX-Detector.

Cell connector ribbons featuring a 130 nm layer of Sn62Pb36Ag2 were attached by manual soldering and the use of soldering flux Kester 925 S. The peel strength was measured by a tensile testing machine from Frolyt. The test is similar to the procedure in DIN EN 28510-1, but is not certified or calibrated. One end of the cell ribbon is clamped to the testing machine, while the cell is mounted in a hold-down unit. The cell ribbon is peeled with a constant speed of 1 mm/s at a constant angle of 90° between ribbon and cell.

3. Results and discussion

To evaluate a possible adhesion promotion by thermal formation of nickel silicide, measurements of fully plated NiCuAg-stacks without a silicidation step were done. Fig. 2 shows the peel force diagrams. As a reference a screen printed sample is shown as the typical level that module producers will ask for.

Microstructural analysis confirmed that introducing a thermal step between nickel- and copper plating successfully leads to the formation of a silicide phase. But even after silicide formation insufficient adhesion is found as can be seen in an exemplary peel force diagram in Fig. 2 (red curve).

The diagram of the screen printed reference shows the breaking force of the wafer itself, rather than true metal peel force. The metal adhesion is shown to be greater than the cohesion of the silicon wafer including its rear side aluminium metallization.

The origin of this low adhesion is investigated in the following by microstructural analysis of the interfaces. It has to be noted that only a small fraction of the contact can be investigated by cross section imaging, and that an even smaller part of each cross section can be shown on the SEM images, which have been chosen to be the most representative for the findings of all prepared cross

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