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Zincate processes for silicon solar cell metallization

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ABSTRACT

To allow plating on aluminum, zincate processes are introduced in metallization of silicon solar cells. Different zincate solutions are investigated regarding their adhesion on typical solar cell surface morphologies. Sufficient adhesion (> 1.5 N/mm) on PVD aluminum layers is demonstrated by zincate processes with subsequent plating of nickel, copper and silver on both random pyramid and damage etched surfaces. Small-size (4 cm²) back-contact back-junction solar cells with an aluminum or aluminum-silicon seed layer are successfully processed in this way. On screen printed aluminum, adhesion has been found to be below 1 N/mm. Microstructural investigation of the failure mode reveals that the aluminum peels off the silicon surface in this case.

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1. Introduction

Aluminum is one of the standard materials for the metallization of crystalline silicon solar cells. It is cheap, well conductive, has a high reflectivity and can act as a p-type dopant, e.g. for the formation of a back surface field or emitter in back contact solar cells.

Aluminum rapidly forms a passivating surface oxide layer in ambient atmosphere, which makes it chemically inert. While this is an advantage in terms of corrosion, processes like soldering or plating onto it are prevented. Such processes could extend the applicability of aluminum.

There are plenty of approaches for plating on aluminum, for example direct plating methods of copper, nickel, chromium, tin or zinc and zincate and stannate immersion methods which are described in [1]. The zincate process is the most widely used for plating onto aluminum and has been studied since the 1920s [2]. Since then it has been optimized by various working groups [3–11] to give good adhesion and reproducibility in applications in the electrical or automotive sector. Especially, double zincate processes have been found to improve adhesion [3]. In double zincate processes the first deposited zinc layer is removed, before the aluminum is coated by the second denser zinc layer. In order to plate well adhesive layers on pure aluminum and aluminum alloys, zincate solutions containing for instance iron, nickel or copper have been developed and published [4,8-11]. Copper acts as nucleation seeds for zinc deposition and iron as well as nickel makes the zinc film more compact [8,10].

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Zincate processes are very simple and cheap immersion processes using standard chemicals. For solar applications, the possibilities are as manifold as the use of aluminum. Rear surfaces of PERC or PERT cells, back-contact back-junction cells with aluminum contact layer or even screen-printed back surface field (BSF) cells could profit from the possibility of plating onto aluminum. These applications represent different requirements for the zincate process; different silicon surface morphologies (e.g. random pyramids and damage etched) are combined with either physical vapor deposition (PVD) or screen-printed aluminum layers.

The objective of this study is to assess the applicability of different zincate processes onto such surfaces in general and with a special focus on the resulting adhesion of the deposited metal stack to the aluminum surface.

2. Experimental

Due to the different applications of zincate in solar cell metallization, silicon wafers with different silicon surface morphologies were produced. These were damage-etched and random pyramid silicon surfaces, which were covered by a PVD aluminum layer $(1\,\mu m$ thick) and surfaces on which an aluminum paste was printed and fired. The zinc layer which was deposited onto the aluminum layers acted as a base for subsequent plating of a nickel-coppersilver stack.

There are many possibilities of preparing a zincate solution. In this study, three different alkaline zincate solutions were used. The first zincate solution (Plain Zincate) consisted only of zinc oxide (ZnO), sodium hydroxide (NaOH) and potassium sodium tartarate (KNaC₄H₄O₆). The two other alkaline zincate solutions were commercial ones. One of these (Iron Zincate) additionally

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contains iron (Fe) and the other one (Multi-Metal Zincate) iron (Fe), nickel (Ni) and copper (Cu). The main experimental objective was the development of a simple and short duration zincate process as a base for subsequent plating. Different process sequences with various immersion times in acidic and alkaline solutions were tested. The parameters which resulted in best adhesion were chosen for following processes. The immersion time of each step was kept below 60 s. The process sequence listed in Fig. 1 was applied.

First the deposited aluminum on different silicon surfaces was structured with a resist, to obtain busbar openings of 1.5 mm for the zincate process to allow subsequent solder and peel testing. The samples were cleaned in nitric acid (HNO₃) for a few seconds. Then the first zincate step was done, which resulted in a spongy and granular crystalline zinc layer. This layer was removed by a second nitric acid (HNO₃) step. Due to these steps the aluminum surface is roughened and the surface area is increased, whereby there is more active area for the following second zincate step available. The increased surface area yielded more finely crystalline and homogeneous zinc deposition. The reaction equations shown in Fig. 2 describe the procedure that takes place in the alkaline zincate solution (left, middle) and in the etching nitric acid (right).

After the second zincate step the resist was removed, because only the zinc area is active for subsequent plating. At this point, adhesion testing by tape test was done. In this way the zincate process was optimized regarding the adhesion of the zinc layer. A single zincate step did not result in zinc layer which passes the tape test, so the double zincate process was carried out for the following samples.

The resist was then removed and the samples were nickel plated. Homogeneous and well adhesive nickel layers were formed by electroless nickel plating as well as by nickel electroplating. Copper and subsequently silver were then electroplated onto the nickel layer. After that, ribbons were soldered onto the silver and the samples were ready for quantitative adhesion test. In order to measure the adhesion between ribbon and silicon, a 90° peelforce-tester was used.

For detection of the quality of deposited zinc layers and following electroplated layers SEM analysis was used. Additionally, ion polishing with subsequent SEM and EDX analyses was done in order to analyze the cross-section of the deposited layers. These methods allow drawing conclusions regarding the performance of each layer.

ICP-OES (inductive coupled plasma-optical emission spectrometry) measurements were made to detect dissolved metals in the used solutions, to analyze deposition and dissolution mechanisms that take place during the zincate and plating processes.

3. Results and discussion

3.1. Zincate processes for PVD aluminum on random pyramid surfaces

First zincate processes were tested on monocrystalline alkaline textured silicon surfaces which were covered by PVD aluminum. Such random pyramid surfaces are typical for solar cells and represent a realistic application (e.g. areas of back-contact backjunction cells or even simultaneous zincating of front and rear metal of the solar cell). Compared to a planar surface, the surface area of this aluminum layer is approximately twice as high.

In spite of the large surface area, the single zincate process does not result in a sufficient adhesion. Therefore, the double zincate process, which was described before, was implemented. In this overall process the first deposited zinc layer (Fig. 3 upper right) is



Fig. 1. Process sequence of samples for adhesion tests.



Fig. 2. Schematic depiction of zincate reaction steps. Left: dissolution of aluminum oxide. Middle: dissolution of aluminum and deposition of zinc. Right: etching of zinc layer.

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