Electrochemical Contact Separation for PVD Aluminum Back Contact Solar Cells

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Abstract

This work deals with a possibility to simplify the processing of back-contact back-junction solar cells. A novel metallization process without using any additional mask is presented. The main focus is set on the contact separation resulting in the interdigitated metal pattern. In case of using evaporated aluminum as contacting material to silicon, aluminum anodizing is a convenient process to convert electrically conductive aluminum to electrically isolating aluminum oxide. In the established processes in which anodizing of aluminum is used for aluminum structuring, masks are used to achieve local anodized areas. In order to make the contact separation process by anodizing more economic, several in-situ anodizing processes either using structured processing units or printing techniques are developed and tested.

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Peer-review under the responsibility of Gunnar Schubert, Guy Beaucarne and Jaap Hoornstra

Keywords: Aluminum; aluminum oxide; anodizing; contact separation; back contact solar cells

1. Introduction

It is generally known that back contact solar cells reach very high efficiencies due to reduced shading by the missing front side grid. An efficiency difference of ~1.5-2 % compared to n-type solar cells with front side grid for the next

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years is speculated by the ITRPV-Roadmap [1]. The potential of the back contact approach for heterojunction solar cell concepts is demonstrated by Panasonic Corp. with a cell efficiency of 25.6 % on 143.7 cm² wafers at research level [2]. Industrial back contact solar cells fabricated by SunPower Corp. achieved a confirmed top cell efficiency of 25.0 % [3]. In order to establish back contact solar cells at the photovoltaic market, there are two essential factors. One factor is reaching the high efficiency level of the above mentioned references and the other is reducing the process costs. Especially the metallization process, for instance the process described by Mulligan [4], is costly for currently manufactured back-contact back-junction solar cells, because complex resist printing and metal etching steps are necessary. Therefore, developing simpler and similarly effective metallization processes for back-contact solar cells is essential. A possible process to reduce processing cost will be discussed in this work. It is a local anodizing process converting PVD deposited aluminum into aluminum oxide, resulting in electrically separated aluminum areas. Aluminum can be employed in back-contact back-junction solar cells to establish the electrical contact to p- and n-doped silicon areas [4]. The anodizing process does not need any resist or etching solution and is a fast process. After contact separation, the anodized aluminum in the gap between p-type and n-type aluminum contacts acts as plating mask, whereby only the aluminum areas (p- and n-contacts) are thickened by plating, using a zincate process [5].

2. Experimental

In order to investigate the different approaches for electrochemical contact separation, conventional Cz silicon wafers were used. An aluminum layer of 1 μm thickness was evaporated on top of a 70 nm SiNx dielectric layer. The thicker the aluminum layer, the more challenging is it to anodize it locally completely in short time (within seconds). A successful process on 1 μm aluminum layer is therefore considered to demonstrate the viability of the approach in combination with zincate processing subsequent plating. Sulfuric acid solution was used as electrolyte. The solution was only applied to the metallic stamp approaches, as discussed in section 3.3. In order to apply the electrolyte by electrochemical dispensing and screen printing approach, the viscosity of the electrolyte has to be increased to reach a defined print layout. Xanthan gum is added to the acidic solution in order to get a paste-like electrolyte which is free from particles.

3. Anodizing of aluminum

3.1. Process in general

The anodizing process enables the conversion of aluminum to porous aluminum oxide. To realize this formation, an inert cathode, an aqueous electrolyte and an aluminum work piece which forms the anode is used, as depicted in fig. 1. By applying an electrical current, two main reactions take place at the electrodes shown by the reaction equations in fig. 1. At the surface of the inert cathode, hydrogen forms due to the presence of electrons. The desired reaction is oxidation of aluminum at the surface of the anode. This reaction results in a porous aluminum oxide layer. The hexagonal shaped Al₂O₃ structure obtained by this process was first described by Keller in 1953 [6]. During the following years, the process was industrially transferred and is used for many applications today. For example, aircraft and automotive industry make use of the anti-corrosion property of anodized aluminum oxide. The porous structure is beneficial for color coating approaches and as template for nanowire formation. The electronic isolating nature of anodized aluminum oxide is employed by the electronics industry.

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\begin{align*}
\text{Cathode:} & \quad 6 \text{H}_2\text{O}^+ + 6 e^- \rightarrow 3 \text{H}_2 + 6 \text{H}_2\text{O} \\
\text{Anode:} & \quad 2 \text{Al} \rightarrow 2 \text{Al}^{3+} + 6 e^- \\
& \quad 2 \text{Al}^{3+} + 9 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6 \text{H}_3\text{O}^+ \\
\text{Overall:} & \quad 2 \text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2
\end{align*}
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Fig. 1. Schematic anodizing process of an aluminum part.
Electrically conductive and isolating materials are also used for photovoltaic manufacturing. Therefore, conductive aluminum which may be locally transformed into isolating aluminum oxide is of special interest.

3.2. Local anodizing by masking

The idea of using anodic aluminum oxide for contact separation of back contact solar cells was first discussed by Verlinden in 1988 [7]. It is an alternative process to the separation of p- and n-contact by chemical etching. The anodizing approach on silicon substrates is also described by Lu [8] and Park [9]. For all of these approaches, masks are necessary to prevent defined aluminum areas from oxidation. By doing this, very narrow oxidized lines are reached [9], however there are difficulties to control that process. The main problem of using organic masks is their adhesion to the aluminum surface. Undercutting is a phenomenon which is well known by etching processes in which local areas are covered by an etching resist. The etching reaction does not only take place in vertical direction but also in horizontal direction under the resist. This phenomenon is more pronounced for the anodic anodizing process, because the anodizing process requires a conductive path to transport the current. If the not masked areas are anodized at the surface, the aluminum becomes electrically isolating. Therefore, the current preferably flows along the path of least resistance which is the aluminum area under the resist in this case. For this reason and due to local heating, the resist may lose adhesion. By adapting the anodizing parameters (e.g., lowering the process speed), the adhesion of the resist could be improved. However, this approach to solve the problem results in a time-consuming process which makes the process unattractive for industrial implementation in solar cell manufacturing. On this account, several maskless approaches for local anodizing are discussed and first test results are presented in the following.

3.3. Local anodizing by structured cathode

One idea to implement local anodizing of thin aluminum layers is a structured metallic cathode consisting of narrow protruding regions (50 μm). This stainless steel stamp which is shown in fig. 2b is produced by mechanical milling. In order to run the process, the protruding regions are wetted by the electrolyte and the stamp is put on the sample in such a way that the aluminum surface is locally wetted. Thereafter, a voltage is applied between the stamp and the aluminum surface (Fig. 2a). As soon as the metal stamp gets close enough to the aluminum surface that the electrolyte bridges the gap between the two metal layers the electrical circuit is closed and triggers the anodizing process to start. The process speed mainly depends on the applied voltage which is adjusted in a way that the anodizing of 1 μm aluminum does not take longer than five seconds.

Also, for this approach there are challenges. One of these is roughness of the metallic protruding regions, which locally form a direct contact to the aluminum surface, resulting in short circuits shown by the processed sample in fig. 2c (red circled areas). Also, non-planarity of both surfaces is critical in this respect. An additional issue is the discussed local heating of the anode and the hydrogen formation at the cathode. Both are resulting in spreading of the electrolyte to unwanted areas. Due to this, also the anodizing reaction is extended to unwanted areas as it becomes visible in the processed sample (Fig. 2c).

![Fig. 2.](image-url) (a) Schematic approach of local anodizing by structured cathode; (b) Mechanical structured cathode (metallic stamp); (c) Aluminum surface which is anodized by the structured cathode approach.
3.4. Local anodizing by local sealing

To overcome the problem that electrolyte spreads to unwanted regions, the metallic stamp is modified by rubber which locally seals the aluminum surface (Fig. 3a). For IBC solar cells, wide lines are sealed by the rubber in this approach (Fig. 3a). For first tests, a rubber cliché of different architecture with only narrow finger structures was used, resulting in residual aluminum lines of ~70 μm width (Fig. 3b). The cross section analysis (Fig. 3b) shows a transition from aluminum to aluminum oxide over a length of ~6 μm. Also, it becomes visible that the aluminum is fully anodized at the not sealed areas down to the underlying silicon. The neighboring aluminum areas are consequently electrically isolated.

A disadvantage of the process is the force which is applied to the wafer in order to get sufficient sealing by the rubber.

3.5. In-situ anodizing by jetting and printing techniques

An alternative contactless process is the dispensing technology which is used in many industrial applications. It is possible to deposit narrow lines of highly viscous media, for instance adhesives, resists and metallic pastes. The dispensing process is well known in the photovoltaic industry as method to deposit conductive metal lines to form the electrode of solar cells [10].

The dispensing technology can simply be modified for the local anodizing approach. In order to achieve this combination, the printing nozzle has to be contacted as cathode as it is shown in fig. 4a. The aluminum surface has to be put on cathodic potential with respect to the work piece that should be anodized. The needed high viscosity of the oxidizing electrolyte medium is achieved in this case by adding thickening agent to the solution. The conductivity can be increased by adding conducting salt. An increased electrolyte viscosity results in lower electrolyte spreading on the aluminum surface and consequently in narrower anodized lines. As soon as the nozzle begins to dispense the viscous acid, the electric circuit is closed which results in the beginning of the electrical anodizing process. The advantage of this kind of approach is the small reaction zone where aluminum is converted to anodized aluminum oxide. The electrochemical process is easy to control and low electrical current is necessary due to the small reaction area.

Some variations regarding the nozzle motion speed, the distance between nozzle and aluminum surface and flow rate of the paste were done. In addition, the electrical parameters in terms of electrical current and potential were varied. Anodized lines of about 200 μm width have been achieved by relatively fast nozzle motion speed of 20 mm/s. The relatively wide lines are resulting from a nozzle opening of 100 μm and can be probably optimized by using a nozzle with a smaller opening, which is ongoing work.
In order to adopt the process to large area solar cells, it is necessary to use multi nozzle dispensing head to realize industrial process speed. In this way it would take about 10 seconds to process one 156x156 mm² wafer. In trying to process a continuous anodized line in terms of an interdigitated back contact structure, line interruptions occurred (Fig. 4c). The main reason for these interruptions was the not yet optimized sulfuric acid paste used in this experiment. There were residual entrapped air bubbles in the paste, resulting in interruptions of the printed line and therefore also interruptions in the current circuit between cathode and anode during the process.

An alternative technique which is established in photovoltaic industry is the screen printing process. It is a widely used processing technology to transfer metallic pastes on silicon substrates. Hence, screen printing of metallic pastes is used as metallization technology for most of the produced both side contacted silicon solar cells. Due to the many years of experience to transfer pastes on silicon wafers by this technique, it is of interest for the anodizing approach. In order to combine the screen printing process with the electrically regulated anodizing process, the standard screen printing setting has to be modified. As in the previously discussed approaches, the aluminum surface is electrically contacted as the anode. The cathode is formed by the screen or by the squeegee alternatively. By pushing the viscous sulfuric acid, which is used as electrolyte, through the screen the electrical contact between the cathode and anode is formed. This results in an anodizing process at the areas, where the aluminum surface is covered by the electrolyte. The electrical anodizing process by screen printing is schematically shown in fig. 5a.

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Fig. 4. (a) Schematic approach of in-situ anodizing by dispensing; (b) Photograph of the electrochemical dispensing process; (c) Image of an anodized interdigitated back contact structure with line interruptions.

Fig. 5. (a) Schematic approach of in-situ anodizing by screen printing; (b) SEM image of an anodized aluminum oxide line, where the aluminum oxide is partly peeled off.
On one hand, an advantage of the process is the very close proximity of cathode and anode, which has the potential to greatly increase the speed as resistive losses in the electrolyte are minimized. However, it is necessary to take care of using a suitable emulsion which has to be sufficiently thick to prevent short circuiting, and chemically resistant against the sulfuric acid electrolyte. In addition, the screen has to be sufficiently electrically conductive to transport the applied electrical current. By optimization of these aspects, first lines are anodized by using the technique. An anodized line, where the formed aluminum oxide is partly peeled off, is shown in the SEM image in fig. 5b. The accurate reason for the peeling aluminum oxide is not clarified yet. Local heating, porosity of Al₂O₃ or the larger volume of aluminum oxide compared to aluminum resulting in mechanical stress after conversion of the aluminum layer might be possible reasons. The phenomenon of flaking aluminum oxide does not affect the quality of the electrical contact separation of the aluminum areas.

4. Conclusion and outlook

Novel approaches for structuring aluminum surfaces in a fast and easy way, are desired. Such processes discussed in this work, could significantly promote novel solar cell concepts like back-contact solar cells, making their production more economic. Four concepts to implement the anodizing process are introduced and discussed. The perspective for successful operation of the process by using the discussed approaches is demonstrated by promising results in first proof of concept experiments using simple experimental setups. Optical inspection, light microscope and SEM analyses were done to characterize the process results.

Up to now, only a proof-of-concept is done for the local anodizing techniques. It has been shown that the techniques are implementable for local anodizing. But there are still challenges to be managed, for instance the optimization of the viscous electrolyte used for the jetting and printing approaches.

By reason of the longtime experience in printing and jetting of metallic pastes for solar cell metallization, preferential treatment will be given to these technologies opposite to the stamp based approaches. Consequently, these printing and jetting processes will be applied to a back contact solar cell metallization process after further optimization.

Acknowledgements

The authors would like to thank Achim Rastelli for the fabrication of the structured cathode and Andrew Mondon for doing cross section SEM analyses. The Fraunhofer-Gesellschaft is acknowledged for funding this preliminary research within the MEF program (project LaCheMA).

References