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Long term stability of copper front side contacts for crystalline silicon solar cells

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ABSTRACT

In this work the long term stability of silicon solar cells with a copper front side metallization based on a fine-line screen-printed silver seed-layer, a plated nickel diffusion barrier, a plated copper conductive layer and a silver capping is investigated in detail. Silicon nitride layers deposited by PECVD or sputtering effectively hinder copper diffusion, which might occur e.g. at contact edges. To investigate the plated nickel diffusion barrier, fast degradation of full size 156×156 mm² cells at elevated temperatures on hotplates and module degradation in the climate chamber executing a damp heat test were performed. Plated nickel thickness influences the degradation speed on cell level. On module level, only the cell without diffusion barrier shows a degradation of 1.2% rel. in efficiency (IEC criteria passed) after 1500 h damp heat test (85 °C, 85% r.h.). The cells with diffusion barrier do not show any degradation. Comparison of cell and module results indicate that fast degradation on hotplates at cell level gives a reasonable first estimate regarding cell degradation due to copper diffusion.

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1. Introduction and motivation

Solar cell metallization is the largest individual cost fraction in the costs of solar cell production, dominated by the front silver metallization costs [\[1\].](#page--1-0) The substitution of the silver with copper $(\sim 100$ times cheaper than silver) offers the potential to reduce the production costs of silicon solar cells significantly. The copper front side metallization, investigated in this work, is based on a fine-line screen printed seed layer, a plated nickel diffusion barrier, a plated copper conductive layer, and a thin plated silver capping [\[2\]](#page--1-0) and offers the advantage of cost reduction by lowering the total front-side silver consumption to $\langle 16 \rangle$ mg per wafer [\[3\]](#page--1-0). Potential weak points in the cell architecture like the SiN_x passivation layer and the plated nickel diffusion barrier may affect the long term stability of such cells and were investigated in this work. A test to characterize the long term stability of cells at elevated temperatures has been suggested by Bartsch et al. [\[4\]](#page--1-0) and were employed to characterize cell degradation due to copper diffusion in [\[5](#page--1-0)–7]. In this work we compare results reached with this fast degradation method on cell level with results of the degradation of single cell modules after 1500 h damp heat testing, which is part of the IEC 61215 accelerated aging standard for PV modules [\[8\].](#page--1-0) This gives an indication about validity of the proposed method. Additionally, potential weak points for copper diffusion in cell and metal contacts were investigated in detail, to assess chances and risks for industrial realization of this metallization architecture.

2. Experimental

2.1. Samples for lifetime measurement

Four inch wafers of 10 Ω cm FZ silicon with random pyramids, 90 $Ω$ phosphorous emitter and different silicon nitride anti reflection coatings on both sides were produced to get symmetrical life time samples. Silicon nitrides with a thickness of 70 nm deposited by PECVD, sputtering and a nitride, deposited using a microwave plasma in an experimental multifunction batch furnace at Fraunhofer ISE, were used. Following silicon nitride deposition the wafers were fired at a set-peak temperature of 900 \degree C in an industrial inline furnace. As reference, samples, passivated with 10 nm ALD aluminum oxide and treated with a FGA anneal (500 \degree C for 10 min), were produced. Photoluminescence and carrier lifetime measurements (QSSPC, Sinton Instruments) were done. Subsequently 200–300 nm copper were evaporated in the middle of the wafers on one side and the wafers were exposed to 300 \degree C for 500 h on a hotplate, to accelerate potential copper diffusion into the device. From previous [\[3\]](#page--1-0) and current (see below) solar cell degradation experiments, this thermal load is considered to be sufficient to simulate the copper diffusion during a typical module lifespan. After temperature treatment the copper was removed by

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wet chemical etching (Piranha etch, 10 min) and the wafers were again characterized by carrier lifetime measurement and photoluminescence Fig. 1.

Fig. 2 shows the experimental sequence. The pre-treatment before copper evaporation was varied using a HF-Dip (1%, 30 s), a dry screen printing step (100 N squeegee-pressure) and wafers without pre-treatment. The screen printing pre-treatment was done at a half automated screen-printing machine using the same equipment (chuck, screen and squeegee) and conducting the same handling as for standard solar cells to include typical potential damage to the silicon nitride into the simulation. The objective of the pre-treatment variation was to evaluate if these procedures that resemble typical stresses to the ARC in production sequences

Fig. 1. Microscope cross section image of the copper metallization contact structure based on a fine line silver seed-layer with a focus on the edge region where the copper layer overlaps the plated nickel diffusion barrier.

can damage the silicon nitride in a way that allows copper to migrate into the junction.

2.2. Solar cell samples

For the long term stability experiments full size (156 \times 156 mm²), p-type solar cells were produced by screen printing fine-line front-side contacts on textured (random pyramids) Cz silicon wafers with PECVD silicon nitride anti reflection coating, a 90 Ω phosphorous emitter with a junction depth of about 200– 300 nm and a standard aluminum backside with silver pads. A standard H-pattern grid with 90 fingers and 3 busbars (1.5 mm) was screen printed on the samples using a commercial fine line Ag-paste and an industrial, automated inline screen printing machine. The screen openings for the contact fingers were $25 \mu m$ wide. The samples were fired at a set peak temperature of 920 \degree C in an inline furnace. Nickel as diffusion barrier, copper as conductive layer and silver as capping layer were plated on the fired contacts using a single side, light induced plating process on inline machines. During this process the backside of the cells does not get in touch with the electrolyte. The nickel mass was varied from 10 mg per cell to 40 mg per cell, corresponding to nickel layer thickness of $0.1-0.6 \mu m$ at the middle of the busbar, which is known to be the part with the lowest nickel plating. The nickel layer at the edges of the cell and at the contact fingers will be considerably higher. The copper layer was 85 mg for each cell, corresponding to a thickness of \sim 8.5 μ m. Also wafers without any diffusion barrier and without copper were produced as reference.

Fig. 2. Schematic drawing of the experimental sequence to characterize the copper diffusion through different silicon nitride layers.

Fig. 3. Photoluminescence images of the life-time samples (without pre-treat) with different silicon nitride layers before and after copper treatment. Only for aluminum oxide a decrease in the carrier life-time can be observed.

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