RIBBON GROWTH ON SUBSTRATE AND MOLDED WAFER - TWO LOW COST SILICON RIBBON MATERIALS FOR PV

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ABSTRACT

This paper focuses on two very promising silicon ribbon materials currently produced for research: Ribbon Growth on Substrate (RGS [1]) by ECN Solar Energy and Molded Wafer (MW [2]) by GE Energy. Both materials are investigated in terms of solar cell processing and characterisation. First cell results of large area 10x10 cm\textsuperscript{2} RGS cells are presented as well as results from 5x5 cm\textsuperscript{2} cells processed from 8x12 cm\textsuperscript{2} RGS and 12.5x12.5 cm\textsuperscript{2} MW wafers.

INTRODUCTION

In consequence of the material production principle of RGS and MW respectively the throughput is very high for both materials compared to other silicon ribbon materials like String Ribbon or EFG. As a consequence the crystal quality suffers from higher crystal defect densities such as dislocations, grain boundaries or impurities incorporated by the crucible, casting and substrate material which limits the minority charge carrier lifetime of the materials. To overcome this limitation the applied adapted industrial screen printing process ensures a sufficient bulk hydrogenation. The wafer width is scalable in a wide range up to 15.6x15.6 cm\textsuperscript{2} for both materials limited only by the substrate sizes used.

CELL PROCESS

RGS and MW wafers are currently produced by laboratory scale R&D machines at ECN and GE respectively and processed at the University of Konstanz (UKN) according to an industrial type screen printing process presented below.

Before processing RGS wafers at the University of Konstanz the uneven front surface of the wafer is leveled using a wafer dicing saw in combination with a special planarization tool. The saw damage (RGS) respectively the defect rich top level of the wafer (MW) is removed by acidic polish etching. The etching step can be either replaced or combined by the application of a chemical surface texture. Next, a 50 Ω/sq. emitter is formed by POCl\textsubscript{3} diffusion. An optional microwave-induced remote hydrogen plasma (MIRHP) step passivates bulk defects followed by the deposition of a hydrogen-rich PECVD SiN\textsubscript{x} layer, which acts as single layer antireflective coating. After screen-printing of front and backside metallisation a cofiring step forms the electrical contacts as well as an aluminum back surface field. During the high temperature cofiring step, hydrogen is again released into the bulk. With this combination of hydrogen treatments (hydrogen originating from the MIRHP passivation as well as from the SiN\textsubscript{x} layer) an optimized passivation of bulk defects is ensured. Ege isolation was performed with a wafer dicing saw.

COMPARISON OF RGS AND MW

The most common advantage of RGS and MW is the scalability of the producible wafer size due to a horizontal growth technique and, as a consequence, the very high wafer production speed. The RGS production principle shown in [3] allows due to a decoupling of the crystal growth and the wafer pulling direction a very high wafer production speed of one wafer per second (650 cm/min). The produced wafer size depends thereby only on the dimensions of the used casting frame and substrate plate. This allows the direct production of silicon wafers of the desired size and thickness. The wafer thickness depends on the wafer pulling speed and can be adjusted in a wide range between 100 µm and 500 µm. The wafer dimensions currently produced by the laboratory scale R&D machine are 8x13 cm\textsuperscript{2} and 10x10 cm\textsuperscript{2}.

MW on the other hand is produced by melting silicon on a substrate plate [2]. The produced wafer size results from the dimensions of the used substrate like in the case of RGS. The wafer thickness can be
adjusted by the amount of silicon used for crystallisation as well. Currently 20x20 cm$^2$ wafers with a thickness in the range of 500 - 700 µm are produced. The wafers are grown in a horizontal configuration (300 cm/min) [5] allowing a similar pulling rate compared to RGS, which is more than two orders of magnitude higher than for a vertical configuration like SR and EFG for instance. Due to the rapid crystal growth and the direct contact of the liquid silicon with the substrate material the fine grained crystal with grain sizes in the range of 100 µm to 1 mm for RGS [6] and 100 µm to 5 mm for MW [5] is usually afflicted with a high dislocation density and impurity concentration for both, RGS and MW. The major impurities are oxygen and carbon [4,5]. The overall oxygen content could be lowered for current RGS material due to a rebuilding of the laboratory scale R&D machine and ranges in the order of standard multicrystalline cast material [7]. The lowered oxygen content is accompanied with an enhancement of the diffusion length and the short circuit current density compared to older RGS material. Due to the slower crystal growth MW shows beside a slightly larger grain structure an oxygen denuded zone near the wafer top surface whereas carbon is distributed homogeneously across the entire wafer thickness. The precipitation of oxygen and carbon however can be suppressed by annealing the MW material which generates a wide precipitate denuded zone near the wafer top surface. As a consequence the lifetime of the material is enhanced [8, 9].

**MW: AS GROWN AND ANNEALED MATERIAL**

Solar cells were processed from as grown MW material as well at different temperatures annealed MW material. The MW wafers were cut into 5x5 cm$^2$ pieces using a laser. The 5x5 cm$^2$ wafers were processed according to an industrial type screen printing process (Fig. 1). Fig. 2 shows a comparison of the long wavelength IQE for untextured solar cells processed from different MW material according to the screen printing process described above without an additional MIRHP passivation. A clear enhancement of the IQE for the annealed material results in a pronounced enhancement at larger wavelengths for the annealed material.

![Fig. 2: Long wavelength IQE of 3 representative untextured cells processed from different as grown and annealed MW material. The long wavelength IQE shows an enhancement for higher annealing temperatures compared to the as grown material.](image)

**SURFACE TEXTURISATION**

In order to enhance $J_{sc}$ different surface texturisation methods were tested on RGS and MW material. Due to the randomly orientated small grains of both materials only isotropic etching texturisation solutions can be used. Non isotropic (alkaline) etching solutions would preferably etch selected crystal orientations. This would result in a non defined very rough wafer surface resulting in enhanced emitter recombination after POCl$_3$ diffusion.

For MW two different Isotextures were applied: Isotexture 1 (isotropic acidic, HNO$_3$, HF, H$_2$O), developed at UKN and Isotexture 2 (isotropic acidic, H$_2$SO$_4$, HF, HNO$_3$). Fig. 4 shows the $J_{sc}$ values of cells processed from the same MW material (higher temperature annealed) with and without an applied texture.

![Fig. 3: Short circuit current densities of untextured cells produced from different as grown and annealed MW material. The cells processed from the annealed material show the higher $J_{sc}$ values compared to the cells processed from the as grown material.](image)
First experiments did not show an enhancement in cell parameters on MIRHP passivated MW wafers. It is expected that hydrogen diffusion is highly restricted in the oxygen rich MW material. This effect was observed for other oxygen rich materials as well (e.g. RGS [11]). On the other hand, MW wafers show a small oxygen denuded zone of better crystal quality (larger grains) near the wafer top surface and a large oxygen rich zone of moderate crystal quality (smaller grains) [8, 9]. The small range of good crystal quality can be improved most probably less by the MIRHP passivation whereas the remaining fraction should show a more pronounced improvement. The fraction of lower crystal quality however is much larger and thus the effect of an extended MIRHP passivation on the bulk lifetime of MW wafers is currently investigated.

Due to the faster diffusion of hydrogen in low [O_i] RGS the hydrogen originating from the SiNx antireflection coating is sufficiently distributed throughout the entire bulk of the solar cell during the short time period of contact firing. Thus an additional MIRHP bulk passivation shows only a slight improvement in cell parameters on current low oxygen RGS material [7].

**CELL RESULTS**

<table>
<thead>
<tr>
<th>screen printed MW cell</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>as grown / Isotexture 1</td>
<td>4.9x4.9 cm$^2$</td>
<td>533</td>
<td>25.5</td>
<td>68.7</td>
</tr>
<tr>
<td>annealed / Isotexture 1</td>
<td>4.9x4.9 cm$^2$</td>
<td>559</td>
<td>28.5</td>
<td>75.0</td>
</tr>
</tbody>
</table>

Table I: IV data of two of the best textured screen-printed MW cells processed at UKN from as grown and annealed material.

<table>
<thead>
<tr>
<th>screen printed RGS cell</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>low [O]I untexured</td>
<td>4.9x4.9 cm$^2$</td>
<td>580</td>
<td>28.1</td>
<td>75.6</td>
</tr>
<tr>
<td>low [O]I untexured</td>
<td>9.8x9.8 cm$^2$</td>
<td>574</td>
<td>27.9</td>
<td>74.3</td>
</tr>
</tbody>
</table>

Table II: IV data of two of the best screen-printed RGS cells from low [O]I RGS material [7].

Table I shows cell results from as grown and annealed MW material processed without an additional MIRHP passivation. The annealed material shows enhanced cell parameters due to the suppression of precipitation near the wafer top surface and as a result an enhanced diffusion length.

The best 5x5 cm$^2$ cell processed from low [O]I RGS material according to the process shown in Fig. 1 achieved an efficiency of 12.3%. Approximately the same efficiency could be achieved on a large 10x10 cm$^2$ RGS wafer which demonstrates the scalability of the material quality and the solar cell process.

**HYDROGENATION**

Due to the rapid crystal growth and the incorporation of impurities originating from the used substrate material the defect density is comparably high for both materials. Beside a hydrogenation of bulk defects during the cofiring of contacts with hydrogen originating from the hydrogen rich SiN antireflection coating, an additional MIRHP passivation should result in an additional passivation of recombination active defects and subsequently in an enhancement of the minority charge carrier lifetime.
SUMMARY

Two silicon ribbon materials, RGS and MW, are compared. Both materials are produced within a horizontal crystal growth configuration and show a very high crystal growth velocity resulting in a fine grain structure with slightly larger grain sizes for the MW material. Because for both materials the liquid silicon is in direct contact with the substrate material during crystallization, a precipitation of carbon and oxygen is difficult to avoid. The limited diffusion length however could be enhanced significantly by annealing in case of MW or by reducing the interstitial oxygen content in case of RGS. An additional MIRHP hydrogenation step enhances the diffusion length further for RGS and is expected to show an equivalent effect in MW. In order to enhance $J_{sc}$, different surface textures were tested on both materials resulting in a gain in $J_{sc}$ of more than 1 mA/cm$^2$ for both materials. Solar cell efficiencies of at least 12% for both materials could be reached on textured screen printed MW cells as well as on untextured RGS cells. A similar efficiency could be demonstrated on an untextured 10x10 cm$^2$ large area RGS cell. 

OUTLOOK

Due to the production technique MW wafers have up to now a comparably large thickness with a depth dependent material quality which enhances the series resistance and the open circuit voltage of the processed solar cells. This limits the fill factor of the cells and as a result the efficiency. Latest experiments demonstrated the feasibility in producing thinner MW wafers which should lead to higher cell efficiencies. Further on, thinner MW wafers are expected to show enhanced lifetimes after an additional MIRHP passivation due to an effective passivation of bulk defects in the larger fraction of the wafer of lower crystal quality. Up to now only few 5x5 cm$^2$ solar cells were processed at UKN. The ratio of the relatively high cell thickness to the small wafer size is disadvantageous at this connection concerning optimum contact firing conditions. Thus it is expected that an extended optimization of the firing parameters will result in higher fill factors and as a result in higher efficiencies even with the actual MW material. Further on MW wafers show a relatively uneven wafer surface. As a result the SiN antireflective coating deposition as well as the screen printing of the front metallisation are inhomogeneous respectively the front metalisation fingers show interruptions. Both exhibits potential for optimization. Whereas MW solar cells show no shunting the most limiting factor for higher efficiencies for RGS solar cells are reduced fill factors as well but most probably due to carbon related shunts occurring in low [O] RGS material [7] as well as other shunting mechanisms [10]. Efficiencies above 13% should easily be reachable as soon as these material induced shunts can be avoided. One approach hereby is to reduce the carbon concentration in RGS wafer material by using optimised casting and substrate materials, another is to avoid a direct contacting of the shunt current paths by a modified cell process including an adapted emitter formation as well as a partial covering back contact [10].

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LITERATURE