Amorphous silicon oxinitride in silicon thin-film solar cells

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Abstract

Silicon oxide is a promising material for silicon thin-film solar cells. As a doped layer it shows low parasitic absorption while as an intrinsic layer it can be used as a high band gap absorber in multijunction solar cells. Whereas doped silicon oxide layers prepared with CO2 are widely investigated, intrinsic layers and the use of N2O as a source gas for oxygen incorporation in silicon thin-film solar cells have not received much attention yet. Therefore we present the optical and electrical properties of doped and intrinsic silicon oxinitride layers at varying N2O flow as well as their performance in single cells.

We found that p-doped amorphous silicon oxinitride layers enhance the short circuit current and the open circuit voltage of amorphous silicon single cells while the fill factor is reduced due to higher series resistance. When N2O is added to the intrinsic layer of amorphous silicon single cells the cell performance deteriorates drastically which is attributed to increased defect density.

Keywords: solar cell, high bandgap, oxide, nitride, p-doped, intrinsic

1. Introduction

Much effort has been made in the last years do increase the efficiency of silicon thin-film solar cells. A very critical loss mechanism of the solar cell device is parasitic absorption in the doped layers due to the high defect
density. Typically, in production the bandgap is widened by carbon to overcome this problem. In the last years p-SiO\textsubscript{2}:H layers, which show improved performance in solar cells, were also investigated intensively [1-3]. The application of silicon oxide to absorber layers has been considered as well. Simulations show that in triple junction solar cells the band gap of the top cell has to be increased to about 2eV to optimize the efficiency [4]. First experiments show promising results [5-7].

We report on our development of intrinsic and doped hydrogenated amorphous silicon oxinitride (a-SiO\textsubscript{x}N\textsubscript{y}:H) for the use in silicon based thin-film solar cells. Doped a-SiO\textsubscript{x}N\textsubscript{y}:H reveals low parasitic absorption losses and has the potential to increase the open circuit voltage. Intrinsic a-SiO\textsubscript{x}N\textsubscript{y}:H is considered as high bandgap topmost absorber in multijunction solar cells. While silicon oxide layers stemming from the use of CO\textsubscript{2} as process gas have been extensively studied as transparent contacts [1-3, 8-11] little attention has been paid to using N\textsubscript{2}O for the same purpose and for intrinsic layers [12-13]. That is why we present the optical and electrical properties of doped and intrinsic a-SiO\textsubscript{x}N\textsubscript{y}:H layers at varying N\textsubscript{2}O flow as well as their performance in single cells.

2. Experimental methods

Amorphous silicon oxinitride layers were deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) using the Cluster Tool from Von Ardenne with separate chambers for the doped and intrinsic layers. The deposition frequency was 13.56 MHz. The remaining deposition parameters are presented in Table 1. Single layers were deposited on Schott Eco glass and p-i-n single cells on commercial Asahi VU transparent conductive oxide (TCO). Silver back contacts were evaporated onto the layers by electron beam.

<table>
<thead>
<tr>
<th></th>
<th>p-a-SiO\textsubscript{x}N\textsubscript{y}:H</th>
<th>i-a-Si:H</th>
<th>i-a-SiO\textsubscript{x}N\textsubscript{y}:H</th>
<th>n-a-Si:H</th>
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<tr>
<td>(SiH\textsubscript{4}) [sccm]</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>(H\textsubscript{2}) [sccm]</td>
<td>80</td>
<td>200</td>
<td>600</td>
<td>200</td>
</tr>
<tr>
<td>(N\textsubscript{2}O) [sccm]</td>
<td>0-50</td>
<td>0-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B\textsubscript{2}H\textsubscript{6}) [sccm]</td>
<td>32</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(PH\textsubscript{3}) [sccm]</td>
<td></td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P [W]</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>p [mbar]</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>d\textsubscript{d} [mm]</td>
<td>25</td>
<td>15</td>
<td>20</td>
<td>20</td>
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<tr>
<td>T\textsubscript{sub} [°C]</td>
<td>220</td>
<td>220</td>
<td>220</td>
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</tr>
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</table>

The optical Tauc bandgap of the single layers was obtained by transmission and reflection measurements with the UV-VIS-NIR spectrometer Cary 5000 from Varian. Conductivity was calculated from current voltage measurements in vacuum with the electrometer 6517B from Keithley. The light source for photoconductivity was a blue LED. The sample geometry for conductivity measurements is defined by parallel in plane silver electrodes with 1 mm gap width in between. Illuminated current voltage characteristics (IV) were measured with the WACOM dual lamp solar simulator according to standard test conditions (AM1.5G spectrum, 1000W/m\textsuperscript{2}, 25°C). We determined external quantum efficiencies (EQE) from differential spectral response measurements.

3. Results and discussion

3.1. p-doped amorphous silicon oxinitride

Fig. 1a shows the optical Tauc bandgap \( E_{\text{Tauc}} \) for p-doped amorphous silicon oxinitride layers as a function of the N\textsubscript{2}O flow \( \phi(N\textsubscript{2}O) \). \( E_{\text{Tauc}} \) increases linearly from about 1.75 eV to about 2.18 eV when \( \phi(N\textsubscript{2}O) \) is raised from 0
sccm to 50 sccm. This is accompanied by a decrease in dark conductivity by several orders of magnitude as can be seen in Fig. 1b. This is in accordance with the findings of Yoon et al. [12].

![Graph](image1)

Fig. 1. (a) Tauc bandgap of p-a-SiOₓNᵧ:H single layers versus N₂O flow; (b) Dark conductivity of p-a-SiOₓNᵧ:H single layers versus bandgap.

Clearly a tradeoff between bandgap widening and dark conductivity of the p-doped layer has to be found for good cell performance. We chose a p-doped layer with 30 sccm N₂O flow which shows a high Tauc bandgap of about 2 eV and still reasonable dark conductivity in the range of 10⁻⁷ S/cm. With this p-layer we produced a single cell featuring the following layers: Asahi VU/p-a-SiOₓNᵧ:H/i-a-Si:H/n-a-Si:H/Ag. The total thickness of the p-i-n stack is about 400 nm. In Fig. 2a IV measurements of this cell are depicted together with results from a reference cell with no N₂O added to the p-layer. Apparently the addition of N₂O to the p-layer leads to less parasitic absorption losses so that the short circuit current is raised by about 1 mA/cm². This gain in current comes from the blue spectral part where a significant amount of light is lost due to absorption in the p-doped layer with no bandgap widening as demonstrated by the external quantum efficiencies in Fig. 2b. Apart from the gain in short circuit current the open circuit voltage is also slightly increased by widening the p-layer bandgap with N₂O. This phenomenon can be explained by the fact that widening the p-layer bandgap introduces a barrier for the holes which therefore remain longer in the intrinsic layer and increase the charge carrier density as well as the splitting of the quasi Fermi levels before they are extracted. Unfortunately the series resistance of the cell with p-a-SiOₓNᵧ:H is higher than of the reference cell which is indicated by the slope of the IV curve near the open circuit voltage (Fig. 2a). Consequently the fill factor is affected accordingly. Yet as indicated by Yoon et al. [12] this problem may be overcome by increased boron doping of the p-a-SiOₓNᵧ:H-layer. The efficiency of the solar cell can be increased further by an optimized back reflector instead of a pure silver back contact. The results show that N₂O is an alternative process gas for widening the bandgap of the p-doped layer in p-i-n single cells.

![Graph](image2)

Fig. 2. (a) IV curves and (b) EQE of a-Si:H single cells with (N₂O) = 30 sccm) and without (N₂O)=0 sccm) bandgap widening of p-layer.
3.2. *Intrinsic amorphous silicon oxinitride*

The incorporation of oxygen in the absorber layer is a more challenging task than in the doped layers due to the high impact of defects on the device performance. Taking this into account the N$_2$O flow is limited to a maximum of 15 sccm. As shown in Fig. 3a the optical Tauc bandgap of intrinsic amorphous silicon oxinitride layers rises almost linearly with the N$_2$O flow. The gas flow ratios cannot be compared directly to those of the doped layers because different H$_2$ gas flows were used. At a gas flow ratio of $\phi$(N$_2$O)/$\phi$(SiH$_4$) $\approx$ 0.4 ($\phi$(N$_2$O)=15sccm) a Tauc bandgap of about 2.1 eV is reached. In contrast, Das et al. reported a 10 times higher gas flow ratio to achieve the same bandgap with CO$_2$ as a source gas instead of N$_2$O [14]. This might be caused by easier dissociation of N$_2$O than CO$_2$ in the plasma or by additional nitrogen incorporation in the network.

Fig. 3b shows photo and dark conductivity of i-a-SiO$_x$N$_y$:H-layers. Initially photo and dark conductivity rise with the addition of N$_2$O then decrease by several orders of magnitude. The difference between photo and dark conductivity does not change continuously for different Tauc bandgaps. Das et al. observe a similar decrease of photo and dark conductivity with bandgap widening by CO$_2$ addition but the difference between photo and dark conductivity starts to decrease as well at a bandgap of approximately 1.9 eV [14].

We applied the intrinsic amorphous silicon oxinitride layers described above in p-i-n single cells with the following structure: Asahi VU/p-a-SiO$_x$N$_y$:H/i-a-SiO$_x$N$_y$:H/n-a-Si:H/Ag. Fig. 4 shows the IV parameters of these cells. The points correspond to the mean values and the error bars to the standard deviation of several equal cells on one 10cm x 10cm substrate. As can be seen the cell performance deteriorates drastically once N$_2$O is added to the intrinsic layer. The short circuit current is expected to decrease with N$_2$O flow since the layer absorption is reduced with increasing bandgap. But the open circuit voltage is meant to increase with N$_2$O flow because the rise in bandgap should allow for a bigger splitting of the quasi Fermi levels. Since the reduction in open circuit voltage is accompanied by a reduction in fill factor, mainly due to reduced parallel resistance, deep defects seem to prohibit good cell performance when N$_2$O is added to the process gases. These defects are probably introduced by nitrogen into the atomic network. Fourier transformed infrared spectra show overlapping SiO and SiN absorption resonances. Additionally, increased absorption at 2100cm$^{-1}$ is observed showing the poor quality of the material for absorber layers. On the other hand band discontinuities at the interface between the high bandgap p-doped and intrinsic layers also might result in a lower fill factor and open circuit voltage. Authors using CO$_2$ instead of N$_2$O (Inthisang et al. [5] and Sritharathikhun et al. [7]) achieve better results in single solar cells with V$_{oc}$ exceeding 1V. In contrast to the p-doped layer the increased defect density in the intrinsic layer leads to inferior cell performance.
4. Conclusion and Outlook

We found that widening the bandgap of the p-layer with N$_2$O increases the short circuit current and the open circuit voltage of a-Si:H single cells while the fill factor is reduced due to larger series resistance. However this drawback can be overcome by increased boron doping of the p-layer. These results show that N$_2$O is an alternative process gas to the commonly used CH$_4$ or CO$_2$ for widening the band gap of the p-a-Si:H layer.

Electrical properties of intrinsic a-SiO$_x$N$_y$:H single layers for the use as high band gap absorbers seem to improve slightly with the initial addition of N$_2$O. Yet single cell properties deteriorate drastically once N$_2$O is added to the i-layer. Apparently N$_2$O introduces too many defects which could be related to nitrogen incorporation since better results have been shown using CO$_2$ as a source gas instead. Consequently, it will be interesting to investigate the influence of other bandgap widening process gases such as CO$_2$ and CH$_4$ in comparison to N$_2$O.

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References


