Short Communication

Silicon nitride anti-reflection coatings for CdS/CuInSe$_2$ thin film solar cells by electron beam assisted chemical vapor deposition

B. J. STANBERY, W. S. CHEN and R. A. MICKELSEN
Thin Film Technology, Boeing Aerospace Company, P.O. Box 3999, M/S 88-43, Seattle, WA 98124 (U.S.A.)
G. J. COLLINS, K. A. EMERY, J. J. ROCCA and L. R. THOMPSON
Department of Electrical Engineering, Colorado State University, Fort Collins, CO 80523 (U.S.A.)
(Received October 26, 1984; accepted January 2, 1985)

The electron beam assisted chemical vapor deposition of silicon nitride anti-reflection coatings onto thin film CdS/CuInSe$_2$ solar cells and the resultant effects on their performance are reported. In some cases large increases in the short circuit current, open circuit voltage and fill factor were observed. The present results are explained by the usual index matching anti-reflection mechanisms and either the passivation of undesirable shunts or improvement of intrinsic diode characteristics.

The most promising material systems for the realization of high efficiency, low-cost all thin film solar cells are the CdS/CuInSe$_2$ and (ZnCd)S/CuInSe$_2$ heterojunction devices. Solar power conversion efficiencies (air mass 1.5) of 9.4% for the former and 11% for the latter have been achieved in the Boeing Aerospace Thin Film Laboratory with 1 cm$^2$ devices [1]. These high efficiencies were achieved by devices utilizing thermally evaporated SiO$_x$ ($1 < x < 2$) Anti-Reflection Coatings (ARCs). The difficulties of process control and of scaling this ARC technique to the large area high throughput requirements of a thin film manufacturing process have led to the investigation of alternative materials and deposition processes. In order to avoid excessive interdiffusion at the heterojunction, an acceptable ARC process should take place at temperatures below the 225 $^\circ$C utilized for the post-deposition O$_2$ bake, which has been shown to be vital for the achievement of high efficiencies [2].

The electron beam assisted chemical vapor deposition (EBCVD) of Si$_3$N$_4$ films at low substrate temperatures (50 - 400 $^\circ$C) has been reported recently by the Colorado State University group [3, 4]. Those initial experiments include deposition onto aluminum, polycrystalline silicon, and crystalline silicon surfaces. Herein we describe the EBCVD of Si$_3$N$_4$ ARCs onto...
CdS/CuInSe₂ photovoltaic devices and the resultant effects on device performance.

The CdS/CuInSe₂ photovoltaic devices for this experiment were prepared as described in ref. [1]. A gold wire was attached to each Al contact pad with silver-filled epoxy prior to the Si₃N₄ deposition in order to provide electrical contact. The air mass 1.5 solar power conversion performance characteristics were then measured and are given in Table 1 as initial results under the comments column.

### Table 1
Comparative performance of cell test samples for silicon nitride anti-reflection coating by EBCVD (ELH lamp at 100 mW cm⁻², 25 °C)

<table>
<thead>
<tr>
<th>Cell</th>
<th>Eff (%)</th>
<th>I_sc (mA)</th>
<th>V_oc (mV)</th>
<th>FF</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>S30L2B</td>
<td>7.24</td>
<td>31.9</td>
<td>381.5</td>
<td>0.595</td>
<td>Initial</td>
</tr>
<tr>
<td>S30L2A</td>
<td>8.16</td>
<td>35.5</td>
<td>388.4</td>
<td>0.592</td>
<td>After ARC</td>
</tr>
<tr>
<td>S40RA</td>
<td>6.91</td>
<td>31.9</td>
<td>375.4</td>
<td>0.578</td>
<td>Initial</td>
</tr>
<tr>
<td>S40RB</td>
<td>8.04</td>
<td>35.9</td>
<td>388.0</td>
<td>0.577</td>
<td>After ARC</td>
</tr>
<tr>
<td>S40RA</td>
<td>3.86</td>
<td>26.1</td>
<td>303.2</td>
<td>0.488</td>
<td>Initial</td>
</tr>
<tr>
<td>S40RB</td>
<td>5.78</td>
<td>31.0</td>
<td>346.0</td>
<td>0.538</td>
<td>After ARC</td>
</tr>
<tr>
<td>S40RB</td>
<td>3.60</td>
<td>26.8</td>
<td>290.0</td>
<td>0.464</td>
<td>Initial</td>
</tr>
<tr>
<td>S40RB</td>
<td>5.65</td>
<td>31.6</td>
<td>337.4</td>
<td>0.531</td>
<td>After ARC</td>
</tr>
</tbody>
</table>

A calculation of the optimum ARC index of refraction for minimizing reflectance at the CdS/encapsulant interface based on the criteria \( n_{ARC} = (n_{CdS} \times n_{encap})^{1/2} \) yields a value of 1.9 based on assumed values of \( n_{CdS} = 2.45 \) and \( n_{encap} = 1.5 \). In order to achieve this index, EBCVD films depositions were performed [3, 4] with the beam perpendicular to the normal direction of gas flow and parallel to the substrate. Depositions were performed at a 4.5 kV accelerating potential, at beam currents from 10 - 20 mA, and at pressures from 160 - 260 mTorr with a total flow of 120 - 240 sccm of reactants in a 47/1 ratio of (NH₃ + N₂)/SiH₄ and a 1.4/1 ratio of N₂/NH₃. Deposition times for nominally quarter-wave ARC's varied from 12 min at lower flow rates to a minimum of 3 min at the highest flow rates. The cells were maintained at a temperature of 140 - 150 °C during the deposition process.

The results of this experiment are summarized in Table 1. The most striking result was the relative increase of 50% in the efficiency of the poorest cells in the lot. Those cells which were initially fairly good increased the least, showing increases in short-circuit \( I_{sc} \) of 12%, but small (3%) increases in open circuit voltage, \( V_{oc} \), and constant fill factors. In contrast those devices exhibiting poor initial performance had large increases in short circuit current of 18% and increases of 14% in \( V_{oc} \) and fill factor, \( FF \). Such large increases in \( V_{oc} \) and \( FF \) cannot be explained solely by increases in the light-generated current \( (I_{ph}) \) term [5] in the equation...
\[ I = I_0(\exp(C(V - R_s I))) + (V - R_s I)R_{sh} - I_{ph} \] (1)

where \( R_{sh} \) is the shunt resistance and \( R_s \) is the series resistance.

The observed improvements in performance of the initially poor cells appears to be a consequence of both increased \( I_{ph} \) due to the ARC effect and either increased shunt resistance \( R_{sh} \) or changes in the diode parameters \( I_0 \) and \( C \). Since the cells were baked at 225 °C prior to the EBCVD of silicon nitride, we believe it is unlikely that the improved characteristics are a purely thermal effect. The detailed mechanism of this effect, however, is still unknown.

In summary, experiments have been performed to demonstrate the feasibility of depositing silicon nitride anti-reflection coatings onto thin film CdS/CuInSe\(_2\) solar cells by electron beam assisted chemical vapor deposition. The results suggest that this process enhances current by the usual index matching anti-reflection mechanism and in some cases serves to passivate undesirable shunts and improve the intrinsic diode characteristics.

The part of this work conducted at CSU was supported by the National Science Foundation and the Office of Naval Research. K. Emery is an ASM America Industrial Research Fellow.