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<td>Xiao, S. Q.; Xu, S.; Zhou, H. P.; Wei, D. Y.; Huang, S. Y.; Xu, L. X.; Sern, C. C.; Guo, Y. N.; Khan, S.</td>
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Amorphous/crystalline silicon heterojunction solar cells via remote inductively coupled plasma processing

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Amorphous/crystalline silicon heterojunction solar cells via remote inductively coupled plasma processing


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Low-frequency inductively coupled plasma (ICP) has been widely used to deposit amorphous or microcrystalline Si thin films, but the intrinsic drawback namely ion bombardment effect limits its application in Si heterojunction solar cells. In this letter, we redesigned typical ICP and realized a remote plasma deposition with suppressed ion bombardment effect. This remote ICP system enables the synthesis of high quality amorphous Si layers with a compact network and a high hydrogen content (10.5%). By using this remote ICP system, we achieved amorphous/crystalline silicon heterojunction solar cells with an efficiency of 14.1% without any back surface field or textures. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4721642]

Silicon heterojunction solar cells have received a great deal of attention in recent years due to their high conversion efficiency and potential for low production cost. A record efficiency of more than 22.3% for Si heterojunction with intrinsic thin layer (HIT) solar cells has been achieved by Sanyo Electric Company, Ltd.1 To date, the most common technique used to synthesize Si heterojunction solar cells is high frequency (>13.56 MHz) capacitively coupled plasma enhanced chemical vapor deposition (PECVD).1–3 This technique has some disadvantages such as the use of very high frequency and low gas utilization (low deposition rate at high working pressure with high hydrogen dilution). In comparison, low frequency (460 kHz) inductively coupled plasma (ICP) has been increasingly attracting more attention for the growth of amorphous (a-Si:H) or microcrystalline (μc-Si:H) Si thin films due to its unique characteristics of high electron density (~10¹³ cm⁻³ in a few Pa), low electron temperatures, low gas consumption, and the simplicity of the configuration.4–7 However, the Si:H films prepared by typical low-frequency ICP usually exhibit low electrical performance with a low hydrogen content,5–6 and therefore have not been applied to synthesize Si heterojunction solar cells so far. This is closely related to the intrinsic nature of typical ICP, where the thin film growing region is highly close to the centre of high density plasma region. In this situation, the ions will easily bombard on the growing surface and thus result in low quality Si:H films with low hydrogen content.

In this letter, we redesigned the typical low-frequency ICP deposition system and realized a remote plasma deposition by separating the thin film growing region from the high density plasma region. This configuration of remote ICP can effectively reduce the possibility of ion bombardment on growing surface, resulting in a film with high hydrogen content and low density of defects. By using this remote ICP deposition system, we demonstrated amorphous/crystalline Si heterojunction solar cell with a conversion efficiency of 14.1%.

The configuration of typical ICP can be found in our previous studies.4–6 The chamber is made of stainless steel in the shape of a cylinder with a diameter of 45 cm and a height of 30 cm. The distance from the inductive coil to the substrate holder is set at 15 cm. For the remote ICP system, the chamber is enlarged with a height of 60 cm and the distance from the inductive coil to the substrate holder is set at 45 cm. In order to estimate the ion bombardment qualitatively, a Langmuir Probe is placed right above the substrate holder to measure the electron energy distribution function (EEDF). The EEDF can provide electron temperature and electron number density of the plasma reaching the growing surface. For a side-by-side comparison, we employed typical ICP and remote ICP to deposit a-Si:H thin films at 100 °C. Both deposition systems are equipped with a low frequency (460 kHz) RF electrical source. Amorphous/crystalline Si heterojunction solar cells were fabricated on a polished p-type CZ c-Si substrate with a thickness of 300 μm and a resistivity of 1–2 Ω cm. We carefully cleaned all the wafers together using standard RCA procedure;8 the resultant chemical oxide preserves a high-quality c-Si surface until the wafers are etched in hydrofluoric acid (HF) (2.5% in H₂O, 1 min) immediately before loading into the vacuum chamber. This removes the oxide and passivates the surface by hydrogen. After reaching a base pressure below 2 × 10⁻⁴ Pa in the vacuum chamber, all depositions consist of a substrate heating period followed by gas dynamic stabilization and controlled deposition using a shutter. A 6-nm-thick intrinsic a-Si:H layer is deposited onto the silicon wafer, followed by an n-type emitter layer of 9 nm deposited from the SiH₄ + H₂ + PH₃ mixture discharges. The ZnO film with a thickness of about 80 nm acting as the front contact layer and anti-reflection was used to enhance the lateral conductivity and minimize the reflection loss. Finally, a simple heterojunction solar cell structure (2 cm × 2 cm) consisting of Al grid/ZnO/n-a-Si/i-a-Si/p-c-Si/Al was measured under a 100 mW/cm² light source with an AM 1.5-like spectrum.

Fourier-transform infrared (FTIR) absorption spectra were measured to determine the hydrogen content C₄ (%) and the microstructure parameter R. The bonded hydrogen...
content can be calculated from the absorption peak of the Si-H wagging mode at ~630 cm\(^{-1}\) using the following formula:

\[
C_H = \left[ \frac{A_\omega \int \frac{\omega(\omega)d\omega}{\omega}}{A_\omega \int \frac{\omega(\omega)d\omega}{\omega} + N_{Si}} \right] \times 100\%,
\]

where \(\omega_{(\omega)}\) is the absorption coefficient, \(\omega\) is the wavenumber in cm\(^{-1}\), \(A_\omega = 1.6 \times 10^{19} \text{ cm}^{-2}\), and \(N_{Si} = 5 \times 10^{22} \text{ cm}^{-3}\) (the atomic density of the crystalline silicon). The microstructure parameter \(R\) indicating the compactness of Si:H films can be deduced from the ratio of the spectral peaks \(I_{2100 \text{ cm}^{-1}}/I_{2000 \text{ cm}^{-1}}\). Here, \(I_{2100 \text{ cm}^{-1}}\) denotes the integrated infrared absorption peak areas of hydrogen bonded in either multihydrides (SiH\(_2\) or SiH\(_3\)) or internal voids, while \(I_{2000 \text{ cm}^{-1}}\) denotes the integrated infrared absorption peak areas of hydrogen in monohydride bonds (Si-H),\(^{11,12}\) For high-quality a-Si:H, a dominant absorption band around 2000 cm\(^{-1}\) is desirable and, consequently, low R values are required.\(^{12}\)

Figure 1 shows two representative FTIR absorption spectra of a-Si:H films prepared by typical ICP and remote ICP. We estimated the hydrogen content of the a-Si:H films prepared by typical ICP and remote ICP. We estimated the hydrogen content of the a-Si:H films to be about 3.3% for typical ICP and 10.5% for remote ICP from the 630 cm\(^{-1}\) peak. Note that the hydrogen content in the Si:H films deposited by conventional PECVD typically lies in the range of 11%–12%.\(^{13}\) The low hydrogen content in the a-Si:H films prepared by typical ICP indicates a great many of defect densities in the films due to the lack of enough hydrogen to passivate the dangling bonds. In comparison, the remote ICP can produce high quality Si:H films with a high level of hydrogen content, close to that of the Si:H films prepared by conventional PECVD. Furthermore, the estimated microstructure parameter \(R\) for the Si:H films deposited by typical ICP is nearly 1, indicating that the resulted films are porous structures with a high level of microvoids. However, for the Si:H films prepared by remote ICP, the R is about 0.35, implying a more dense lattice network. Also, the disappear of Si-O bonds for the Si:H films prepared by remote ICP means that the resulted films have a more compact network exhibiting an excellent resistance to post-oxidation.\(^{14}\)

From the above results, we can conclude that the configuration of ICP has a critical impact on the properties of resulted Si thin films. In order to further understand what intrinsic natures of ICP determine the thin film properties, we measured the \textit{in-situ} EEDF spectra for three situations with different distances from the inductive coil to substrate holder: (a) typical ICP of 15 cm; (b) intermediate ICP of 30 cm; and (c) remote ICP of 45 cm. The \textit{in-situ} EEDF spectra measured through the Langmuir Probe right above the growing surface for three situations are shown in Figure 2. The electron number density \(n_e\) reaching the growing surface may be extracted from the EEDF spectra as follows:\(^{15}\)

\[
n_e(x) = \int_{0}^{\infty} f_e(x)de_x,
\]

where \(f_e(x)\) is the electron energy distribution function. For typical ICP, the electron number density can reach \(4.6 \times 10^{12} \text{ cm}^{-3}\). It is well known that the plasma region contains electrons, ions, and radicals. Such high density electrons close to the substrate holder indicates a large number of ions near the growing surface. These ions can directly bombard on the substrate and thus result in low quality Si:H films with a low hydrogen content. For intermediate ICP, the electron number density reduces significantly by a factor of 5, indicating that the ion bombardment can be reduced greatly. For remote ICP, however, there is no EEDF signal. This means that the electrons or ions can hardly reach the growing surface in this situation because they will recombine when they diffuse out of the plasma region. Therefore, the ion bombardment effect is suppressed for remote ICP. Nevertheless, the radical species useful for the thin film growth such as SiH\(_2\), SiH\(_3\), and SiH will diffuse to the substrate to promote the deposition. The reduction of ion bombardment effect from typical ICP through intermediate ICP to remote ICP can also be interpreted by the change of sheath layer, which in general sustains intense ion bombardment onto the growing surface. As the electron density near the growing surface decreases significantly, the sheath layer atop the growing surface becomes wider. The associated electric field is thus much weaker to accelerate the ions to the growing surface. To a certain extent, this remote ICP system is quite similar to some reported ICP systems,\(^{16}\) where the thin film growing region is separated from the high density plasma region.

Both dark and photo current-voltage (I-V) curves of amorphous/crystalline Si heterojunction solar cells with a structure of Al grid/ZnO/n-a-Si:H/i-a-Si:H/p-c-Si/Al prepared by remote ICP are shown in Fig. 3. Inset is the schematic structure of the single junction solar cells. As seen, the dark I-V curve shows an extraordinary rectifying behaviour. The low dark saturation current of \(1.3 \times 10^{-6} \text{ A/cm}^2\), extracted from the dark I-V characteristics of the device, leads to an observed fill factor (FF) of 71.0%. We have succeeded in the preparation of good-quality heavily doped n-layers, ensuring an open-circuit voltage \(V_{\text{oc}}\) of 590 mV without any back surface field. It is well known that Si
heterojunction solar cells with a V_{oc} more than 650 mV require a symmetrical structures consisting of a front junction and a back surface field. The short-circuit current I_{sc} of 33.6 mA/cm² also nearly reaches the limit of crystalline Si-based solar cells without any surface textures for light trapping. For comparison, we also synthesized Si heterojunction solar cells using typical ICP system with similar processing parameters. The maximum I_{sc} and V_{oc} can only reach 24.8 mA/cm² and 512 mV, respectively, not to mention the fill factor and cell efficiency. Such low I_{sc} and V_{oc} may be ascribed to the low hydrogen content in the a-Si:H films deposited by typical ICP. For Si heterojunction solar cells, the key to high cell efficiency is the recombination at the a-Si:H/c-Si interfaces: the a-Si:H layers not only induce a band bending but also passivate the front surfaces of the c-Si by saturation of dangling bonds. One more reason may be correlated with the distribution of H atoms in the films. It has been reported that monohydride bonds (Si-H) are more beneficial than multihydrides (SiH₂ or SiH₃) bonds for the surface passivation of c-Si. The compact a-Si:H layer with low SiH₂ bonds and high Si-H bonds prepared by remote ICP can passivate the heterojunction interface effectively and thus leads to good device performance, while the porous a-Si:H layer with high SiH₂ bonds prepared by typical ICP resulted in low solar cell performance. It is worth noting that the representative deposition rate of a-Si:H films is as low as 0.1 nm/s for remote ICP, while that can reach 0.5 nm/s for typical ICP. Since ultrathin layers (10–20 nm) of a-Si:H are required in the fabrication of Si heterojunction solar cells, such low deposition rate for remote ICP may be beneficial for the deposition control.

The huge difference in cell performance of Si heterojunction solar cells prepared by remote ICP and typical ICP can be supported by the following lifetime measurement of p-type c-Si wafers passivated by a-Si:H films deposited by both methods. The effective minority carrier lifetime was

![FIG. 2. The in-situ EEDF spectra for three situations with different distances from the inductive coil to the substrate holder: (a) typical ICP of 15 cm; (b) intermediate ICP of 30 cm; and (c) remote ICP of 45 cm. The electron number density nₑ reaching the growing surface extracted from the EEDF is 4.6 \times 10^{12} \text{cm}^{-3}, 9.6 \times 10^{11} \text{cm}^{-3}, and 0 \text{cm}^{-3} for typical ICP, intermediate ICP, and remote ICP, respectively.]

![FIG. 3. (a) Dark and (b) photo I-V curves for amorphous/crystalline Si heterojunction solar cells with a structure of Al grid/ZnO/n-a-Si:H/i-a-Si:H/p-c-Si/Al synthesized by remote ICP. Inset in (a) is the schematic structure of the single junction solar cells.]

V_{oc}=590 \text{mV}
I_{sc}=33.6 \text{mA/cm}^2
FF=71.0\%
Eff=14.1\%
measured using the quasi-steady state photoconductance decay (QSSPCD) technique. The effective minority carrier lifetime $\tau_{\text{eff}}$ of the double-side passivated c-Si wafer by a-Si:H films for both deposition methods is shown in Figure 4. As shown, the a-Si:H films deposited by remote ICP provide a much better passivation effect for p-type c-Si wafers than that deposited by typical ICP. In particular, the $\tau_{\text{eff}}$ is 490 $\mu$s for remote ICP while that is only 40 $\mu$s for typical ICP at excess carrier density of $10^{15}$ cm$^{-3}$. The maximum surface recombination velocity $S_{\text{eff}}$ estimated from $1/\tau_{\text{eff}} = 2S_{\text{eff}}d$ is 30.6 cm/s and 375 cm/s for remote ICP and typical ICP, respectively. The compact a-Si:H layers with high hydrogen content and high Si-H bonds prepared by remote ICP are responsible for this significantly enhanced passivation effect. It is the enhanced passivation effect that results in better cell performance of Si heterojunction solar cells prepared by remote ICP than that by typical ICP.

We further study the doping ratio effect of n-layer on the performance of Si heterojunction solar cells prepared by remote ICP system. As shown in Table I, both $V_{\text{oc}}$ and FF increase drastically as the doping ratio of PH$_3$:SiH$_4$ increases, reaching a maximum value of 590 mV and 71.0% at a doping ratio of 0.23:5.0. However, as the doping ratio further increases, $V_{\text{oc}}$ decreases significantly while FF slightly changes. No matter how the doping ratio changes, the contact resistance between n-layer and ZnO electrode decreases correspondingly, leading to a decrease in series resistance. Therefore, FF increases significantly with the doping ratio. When the actual doping reaches a saturate value, the contact resistance will hardly change, resulting in a slight change in FF. The little variation in $J_{\text{sc}}$ may be ascribed to the unchanged spectral response, which needs further verification by quantum efficiency measurement.

In summary, we developed remote and low-frequency ICP-CVD system to synthesize Si heterojunction solar cells. The remote ICP can separate the thin film growing region from the high density plasma region and thus effectively reduce the possibility of ion bombardment on growing surface. High quality a-Si:H layers with a compact network and a high hydrogen content were thereby deposited at a fairly low deposition temperature of 100°C. By using the remote ICP system, we achieved Si heterojunction solar cells with an efficiency of 14.1% without any back surface field or textures. This performance promises a significant improvement provided these delicate technologies are consummated in the future.

TABLE I. The performances of Si heterojunction solar cells with a structure of Al/p-c-Si:Si:H (~6 nm)/n-a-Si:H (~9 nm)/ZnO:Al (~80 nm)/Al prepared by remote ICP at different doping ratio of PH$_3$:SiH$_4$.

<table>
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<tr>
<th>PH$_3$:SiH$_4$ (sccm)</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>$V_{\text{oc}}$ (mV)</th>
<th>FF (%)</th>
<th>h (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09:5.0</td>
<td>33.3</td>
<td>447</td>
<td>51.2</td>
<td>7.6</td>
</tr>
<tr>
<td>0.15:5.0</td>
<td>32.7</td>
<td>482</td>
<td>64.1</td>
<td>10.1</td>
</tr>
<tr>
<td>0.23:5.0</td>
<td>33.6</td>
<td>590</td>
<td>71.0</td>
<td>14.1</td>
</tr>
<tr>
<td>0.30:5.0</td>
<td>33.1</td>
<td>507</td>
<td>69.6</td>
<td>11.7</td>
</tr>
</tbody>
</table>

FIG. 4. The effective carrier lifetime as a function of the excess carrier density for p-type c-Si wafers passivated by remote ICP a-Si:H and typical ICP a-Si:H layers.