HIT Solar Cells with n-Type Low-Cost Metallurgical Si

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ABSTRACT. In this study, a conversion efficiency of 20.23% was obtained in a heterojunction with intrinsic thin layer (HIT) solar cell with a metallurgical Si wafer (156 mm × 156 mm). The impurity concentration and compensation level and their effect on the performance of the HIT solar cell with a metallurgical Si wafer were investigated using the AFORS-HET simulation software. It was revealed that a small amount of impurity in metallurgical Si materials did not hamper the solar cell properties.

**Introduction**

The photovoltaic industry is continuously striving to achieve high conversion efficiencies in a cost-effective manner. Heterojunction with intrinsic thin layer (HIT) solar cells enable a high open-circuit voltage and, therefore, a high conversion efficiency owing to the hydrogen-rich a-Si passivation layer on the n-type Si wafer. Panasonic (formerly Sanyo) realized the highest HIT conversion efficiency of 25.6%.1 However, the high manufacturing cost (∼$ 0.5/w) of the HIT solar cells is a bottleneck for further capacity expansion. Currently, solar-grade Si (SOGSi) is mainly fabricated using the improved Siemens method. However, this method involves high energy consumption and high cost and causes pollution. Si purification using metallurgical methods has drawn significant attention in the past decade due to its cost-effectiveness, low energy consumption, and low pollution. Further, n-Type Si prepared using metallurgical methods does not require phosphorus removal by electron beam refining, which is an expensive process, and therefore, the manufacturing cost with this method is only 40% of that with the Siemens method. An et al.2 investigated the main solar cell performance for both the Siemens method and metallurgical methods, and the conversion efficiency for regular monocrystalline metallurgical Si was found to be 18.3%. Further, Einhaus et al.3 reported a cell efficiency of 19% for mono-c UMG n-type Si on a 149 cm2 cell in the first trial using the heterojunction solar cell technology. The automat for simulation of heterostructures (AFORS-HET) simulation software was developed specifically for heterojunction solar cells, and any type of semiconductor tandem materials with random combinations can be simulated using this software. Researchers investigated the HIT solar cell performance using AFORS-HET simulation, and the results were significant [4–6]. In this study, the AFORS-HET simulation was employed to investigate the properties of the HIT solar cell with metallurgical Si. In this study, Si used in the HIT solar cells was fabricated by both the Siemens method and metallurgical method for comparison.

**Materials and Methods**

*HIT solar cell fabrication*

HIT solar cells were fabricated using both Siemens Si and metallurgical Si (n-type Si wafers; 156 × 156 mm2) by ULVAC plasma-enhanced chemical vapor deposition for 5–10 nm a-Si films. A transparent conductive oxide (TCO) was prepared by Sumitomo reactive plasma deposition. Finally, screen printing was applied to form a silver metal contact to extract the light-generated current. The fabricated HIT solar cells had a bifacial structure with four bus bars (Figure 1(a)). The temperature for the entire HIT solar cell fabrication process was less than 250 °C. *I*–*V* parameters were characterized with a Kopel steady-state IV tester.

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| TCO  TCO  a  -  (  Si  i  )  a  -  (  Si  p  +  )  a  (  Si  -  i  )  c-  Si  (  )  n  a  -  (  Si  n  +  )   1. (b)   Figure 1: (a) Front face of the fabricated HIT solar cell. (b) Schematic of the HIT solar cell structure.    Figure 2: Defect state distribution of the different types of a-Si:H layers obtained by simulation. |

*s*

Si materials produced by metallurgical methods have the following properties: (1) impurity compensation effect such as coexistence of B and P and (2) higher concentration of metal impurities such as Fe and Cu impurities. The Fe and Cu concentrations in the Si prepared by the Siemens method are negligible. The metallurgical Si wafers used in this work had a resistivity of 2.0 Ω⋅cm, minority-carrier lifetime of 30 𝜇s, and Fe concentration of 0.005 ppb. The tested parameters of the Si wafers were inputted into the AFORS-HET software to simulate the HIT solar cell. Furthermore, the effect of metal impurity and B and P compensation on the cell properties were investigated. In the AFORS-HET simulation, the doping concentrations of both B and P can be used, and the impurity level can be easily adjusted, which is beneficial for conducting research on compensated HIT solar cells. The HIT solar cell structure for this simulation is p+-a-Si/i-aSi:H/c-Si/i-a-Si:H/n+-a-Si (Figure 1(b)). The simulation parameters were obtained from previous reports7–10 and are listed in Table 1. Owing to the reduction in thickness upon acid etching, the Si substrate (170 𝜇m) used in this simulation was smaller than the bare Si wafer (190 𝜇m). Surface recombination at the a-Si/c-Si interface was 1.0 × 107 cm−1. The defect state6 settings for p+-a-Si, i-a-Si, and n+-a-Si are shown in Figure 2. Light trapping can occur on both front and back surfaces. Both front and back electrodes were in ohmic contact. The reflectivities for the front and back surfaces were 0.1 and 1, respectively. The simulated light soaking conditions were AM1.5 and 100 mW/cm2. The effective wavelength range was 0.38–1.1 𝜇m.

**Results and Discussion**

*Influence of deep energy-level impurity on solar cell properties*

Si purification by metallurgical methods can be realized through gas blowing, slagging boron removal, phosphorus removal by electron beam refining, acid leaching, and unidirectional removal of solidification metals. The repeated processes were applied to remove the metal impurities in Si and meet the requirements for SOG.

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| Table 1: Input parameters for AFORS-HET simulation.   |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | | Parameters | a-Si:H(p) | | a-Si:H(i) | c-Si(n) | a-Si:H(n+) | | Thickness (nm) | 5 | | 5 | 1.7×105 | 5 | | Dielectric constant | 11.9 | | 11.9 | 11.9 | 11.9 | | Electron affinity (eV) | 3.8 | | 3.8 | 4.05 | 3.8 | | Band gap (eV) | 1.70 | | 1.74 | 1.12 | 1.70 | | Effective conduction band density (cm−3) | 1.0×1020 | | 1.0× 1020 | 2.8×1019 | 1.0×1020 | | Effective valence band density (cm−3) | 1.0×1020 | | 1.0×1020 | 1.04×1019 | 1.0×1020 | | Electron mobility (cm2 V−1s−1) | 10 | | 20 | 1040 | 10 | | Hole mobility (cm2 V−1s−1) | 1 | | 2 | 412 | 1 | | Acceptor concentration (cm−3) | 1.0×1019 | | 0 | 5×1015 | 0 | | Donor concentration (cm−3) | 0 | | 0 | 7.03×1015 | 1.0×1019 | | Thermal velocity of electrons (cm/s) | 1.0×107 | | 1.0×107 | 1.0×107 | 1.0×107 | | Thermal velocity of holes (cm/s) | 1.0×107 | | 1.0×107 | 1.0×107 | 1.0×107 | | Layer density (g ∗ cm−3) | 2.328 | | 2.328 | 2.328 | 2.328 | | Band tail density of states (cm−3 eV−1) | 2.0×1021 | | 2.0×1021 |  | 2.0×1021 | | Characteristic energy (eV) for donors, acceptors | 0.045, 0.037 | | 0.045, 0.02 |  | 0.06, 0.037 | | Capture cross-section for donor states, e, h (cm2) | 1.0×10−15, 1.0×10−17 | 1.0×10−15, 1.0×10−17 | |  | 1.0×10−15, 1.0×10−17 | | Capture cross-section for acceptor states, e, h (cm2) | 1.0×10−17, 1.0×10−15 | 1.0×10−17, 1.0×10−15 | |  | 1.0×10−17, 1.0×10−15 | | defect density of states at Gaussian peak energy (eV) | 1.0×1017–6.0×1019 | 1.0×1016–1.0×1019 | |  | 8.0×1017–1.0×1020 | | Standard deviation (eV) | 1.10, 1.35 | 0.725, 1.025 | |  | 0.40, 0.65 | | Capture cross-section for donor states, e, h (cm2) | 1.0×10−14, 1.0×10−15 | 1.0×10−14, 1.0×10−15 | |  | 1.0×10−14, 1.0×10−15 | | Capture cross-section for acceptor states, e, h (cm2) | 1.0×10−15, 1.0×10−14 | 1.0×10−15, 1.0×10−14 | |  | 1.0×10−15, 1.0×10−14 | |

metal impurities in the Siemens Si were higher. The presence of metal impurities (Fe, Cu, and Ni impurities) decrease the minority-carrier lifetime and reduce the light-generated current. In the AFORS-HET simulations, defects can be deliberately added to c-Si for simulating the impact of metal impurities on the solar cell properties. In this work, only Fe and Cu were considered to be the main metal impurities. Owing to the directional solidification of the Fe residues, electron beam processing with copper electrodes can be introduced. The Fe and Cu energy levels in Si were 0.4 and 0.24 eV, respectively. The electron capture cross-sections for Fe and Cu were 4.5 × 10−14 and 1 × 10−14 cm−2, respectively,10 while the hole capture cross-sections for Fe and Cu were 6.91 × 10−17 and 1.8 × 10−17 cm−2, respectively. First, we considered only the Fe impurities and set the concentration range as 1 × 1010–1 × 1015 cm−3. The solar cell properties are shown in Figure 3(a). It is evident that the density of defect states should be less than 1012 cm−3 to achieve a good performance. When it is higher than 1012 cm−3, the cell properties are drastically affected by the defect state, and the conversion efficiency drops below 20%. Meanwhile, the short-circuit current density (𝐽sc) and open-circuit voltage (𝑉oc) decrease. For instance, when the Fe impurities increase up to 1015 cm−3, 𝑉oc decreases to 468 mV, 𝐽sc 2 drops to 24.21 mA/cm, and the conversion efficiency is only 8.07%. Figure 3(b) shows the simulation results in the presence of both Fe and Cu impurities. During the simulation, the concentration of the Fe impurity was fixed at 1012 cm−3, while the concentration of the Cu impurity was varied from 1 × 1010 to 1 × 1015 cm−3. Consequently, when the Cu concentration was higher than 1012 cm−3, the conversion efficiency (𝜂) dropped to less than 20%. The cell performance deteriorated with increasing concentrations of the Cu impurities. The data in Figure 3(a) and 3(b) suggest that the effects of an individual impurity are added to each other when there are multiple impurities. The main impurities in the metallurgical Si material are Fe and Cu. In the present study, the Fe and Cu concentrations measured by glow discharge mass spectrometry (GDMS) were 2.6 × 1012 and 6.5 × 1011 cm−3, respectively. Using the measured impurity data as inputs in the AFORS-HET software, the simulated 𝑉oc, 𝐽sc, fill factor (FF), and 𝜂 were determined to be ~2684.1 mV, ∼39.89 mA/cm, ∼75.08%, and ∼19.58%, respectively.

*Influence of compensation level on solar cell properties*

In metallurgical n-type Si wafers, there is a certain amount of B doping in addition to P doping. This is a well-known compensation phenomenon, and the compensation is proportional to the B concentration. In the AFORS-HET simulation, donor concentration 𝑁𝐷 and acceptor concentration 𝑁𝐴 can be inputted simultaneously. The carrier mobility is inputted manually as a fixed parameter, as the carrier mobility at different doping concentrations is different. At room temperature, the carrier mobility in Si can be described using the following set of equations:11

(1)

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| (a) Fe (b) Fe+Cu  Figure 3: Effect of (a) Fe impurities and (b) Fe and Cu impurities on the cell properties. |

Equation (1) reflects the concentration of donor and acceptor impurities at room temperature. To simulate the compensation effect on the cell properties more accurately, the difference between 𝑁𝐷 and 𝑁𝐴 was calculated and found to be 2.03 × 1015 cm−3. The acceptor concentration, 𝑁𝐴,varies from 1 × 10 to 2 × 10 cm. Electron mobility and hole mobility were calculated using the MATLAB software and inputted into the AFORS-HET software for simulation. The simulated results are shown in Figure 4. It can be seen from Figure 4 that the influence of compensation on the cell properties was minor. Nonetheless, higher the compensation, poorer were the cell properties. 𝑁𝐴 for metallurgical Si, as measured by GDMS, was found to be 1.368 × 1015 cm−3.

*Comparison of simulated and measured solar cell properties*

In this work, 156 mm × 156 mm metallurgical Si wafers were used to fabricate HIT solar cells in a pilot line at the Shanghai Institute of Micro-System and Information Technology, Chinese Academy of Sciences. For comparison, the same process was used to fabricate a batch of Siemens Si HIT solar cells. The *I–V* curves of both the types of HIT solar cell are shown in Figure 5.

The measured parameters of metallurgical Si were introduced into the AFORS-HET software for simulating the HIT solar cells. Table 2 shows the simulated and measured cell properties for comparison. The measured and simulated 𝑉oc, 𝐽sc, FF, and 𝜂 values for the HIT solar cells were similar. However, the simulated temperature coefficient (TC) of the photoelectric conversion efficiency was lower than the measured value. With AFORS-HET software optimization, 𝜂 of the HIT solar cell with metallurgical Si increased up to 21.17% when the density of defect states was 1012 cm−3 and the concentration of B was zero. Table 2 also shows a comparison of the performance of the cells fabricated using metallurgical Si and Si prepared by the Siemens method in the same batch. The electrical properties of the former were slightly poorer than those of the latter. However, due to the significantly low cost of metallurgical Si materials, the performance to cost ratio for the metallurgical Si HIT solar cells would be higher than that of Siemens Si solar cells. This suggests that the metallurgical Si HIT solar cells have a significant potential for large-scale industrial manufacturing.

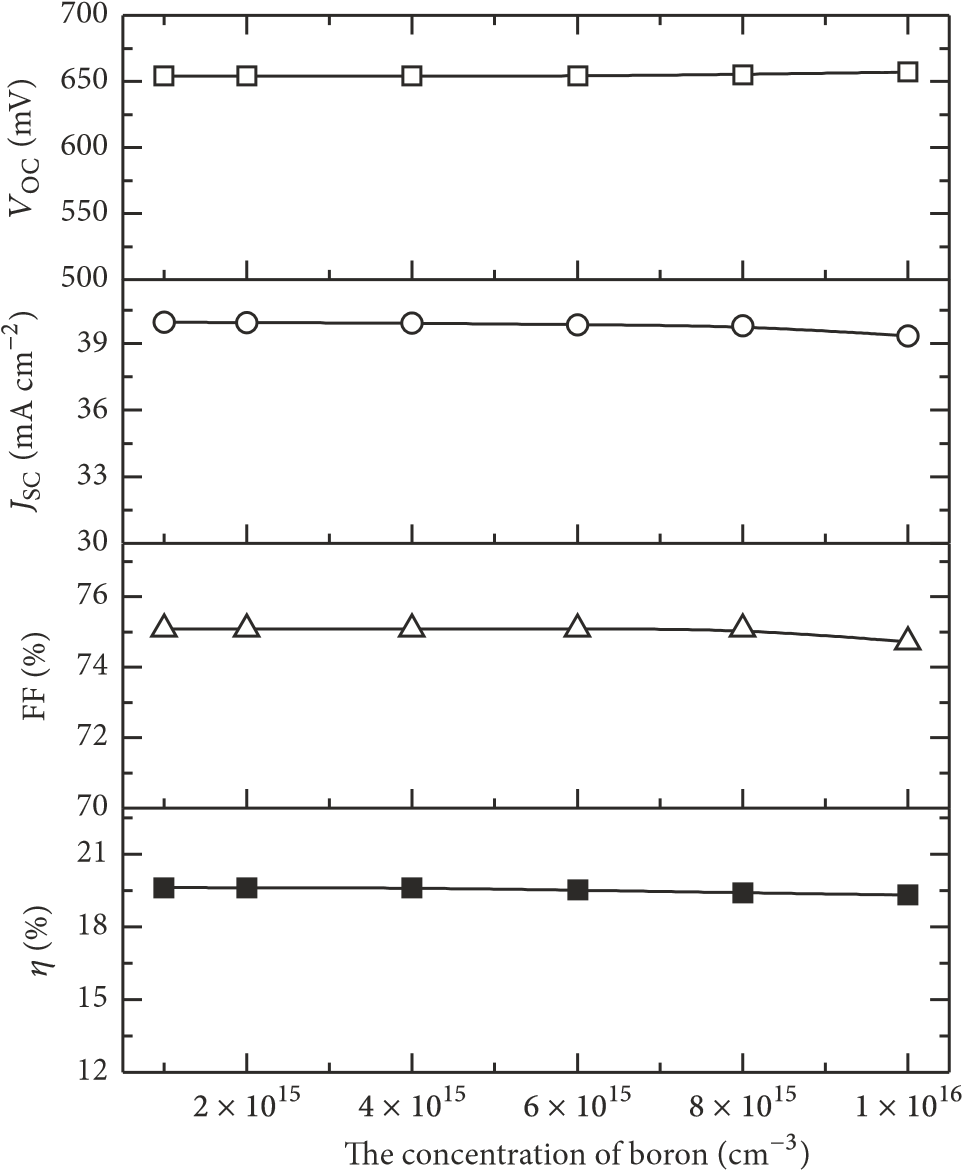
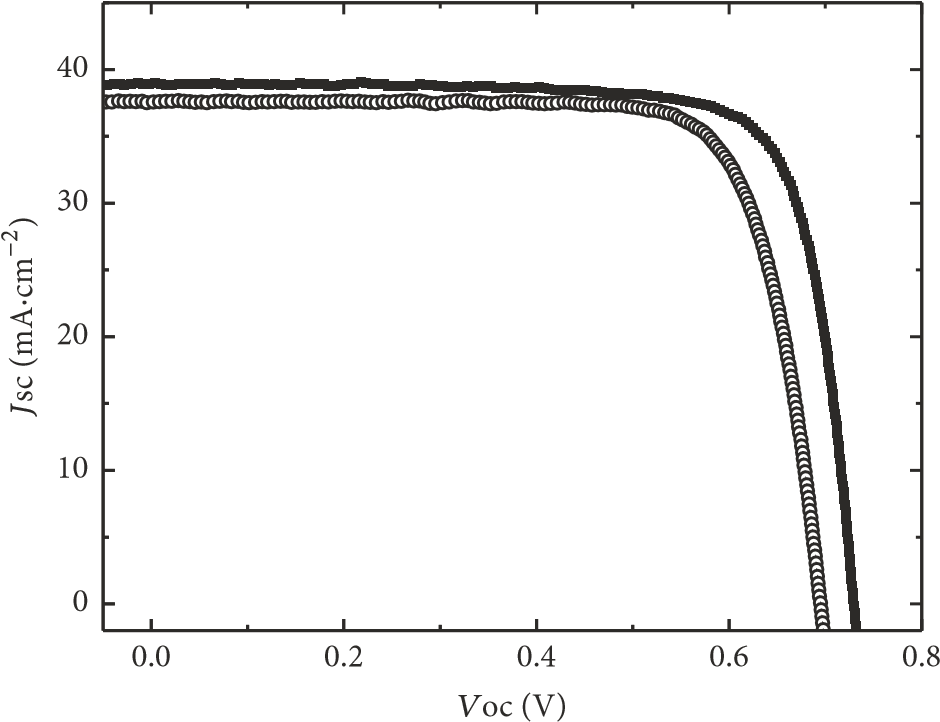


Figure 4: Influence of compensation level on the solar cell properties.

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| Table 2: Comparison of HIT solar cell properties with metallurgical Si and Siemens Si.   |  |  |  |  |  | | --- | --- | --- | --- | --- | | Cell parameters | Siemens Si | Metallurgical Si | Simulated data | Optimized data | | 𝑉oc (V) | 0.7294 | 0.6949 | 0.6841 | 0.7061 | | 𝐽sc (mA/cm2) | 38.918 | 37.564 | 37.656 | 39.641 | | FF (%) | 78.37 | 77.48 | 75.08 | 81.08 | | 𝜂 (%) | 22.25 | 20.23 | 19.58 | 21.17 | | TC (%/∘C) | −0.225 | −0.3043 | −0.2000 | −0.2000 | |



Metallurgical Si

Siemens Si

Figure 5: *I-V* curves of HIT solar cells fabricated using metallurgical Si and Siemens Si.

**Conclusions**

In summary, it can be concluded that despite the marginally poorer material quality of metallurgical Si compared to that of Siemens Si, HIT solar cells with competitive performance can be fabricated using the former. The best performance of the metallurgical Si HIT solar cell corresponded to 𝑉oc, 𝐽sc, FF, 𝜂, and TC of ∼694.9 mV, ∼37.564 mA/cm2, FF ∼77.48%, ∼20.23%, and ∼ −0.3043%/∘C, respectively. AFORS-HET simulation studies revealed that a small amount of impurity in metallurgical Si materials did not hamper the solar cell properties.

ASSOCIATED CONTENT

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Author Contributions

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Notes

The authors declare that they have no conflicts of interest.

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