Improvement of a-Si$_{1-x}$Ge$_x$:H single-junction thin-film solar cell performance by bandgap profiling techniques

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ABSTRACT

In this work, the effect of hydrogen dilution on the Ge content of the film and the effect of bandgap grading in the a-Si$_{1-x}$Ge$_x$:H absorber near the p/i and the i/n interfaces on cell performance were discussed. The a-Si$_{1-x}$Ge$_x$:H single-junction solar cells were improved by employing both p/i grading and i/n grading. The i/n grading increased the V$_{OC}$ and the FF while it also reduced the J$_{SC}$ as compared to the cell without grading. Presumably the potential gradient established by the i/n grading facilitates the hole transport hereby improved by the FF. On the contrary, the potential barrier established by the p/i grading seemed to limit the cell performance and constrain the p/i grading width below 20 nm due to the drop in FF and J$_{SC}$. Combining the effects of bandgap grading on the V$_{OC}$, J$_{SC}$ and FF, the suitable thicknesses of the p/i and the i/n grading were 20 nm and 45 nm, respectively. Finally, the grading structures accompanied with further optimization in doped layers were integrated to achieve a cell efficiency of 8.59%.

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) based thin-film solar cells have progressed in the past few decades. Guha et al. have achieved an initial efficiency of 14.6% by a multi-gap amorphous silicon based solar cell in 1997 [1]. Hydrogenated amorphous silicon germanium (a-Si$_{1-x}$Ge$_x$:H) has proved to be a promising material for the low-bandgap cell application in the multi-junction structure [2]. The composition of a-Si$_{1-x}$Ge$_x$:H material affects its optoelectronic properties significantly. Generally, the incorporation of Ge narrows the bandgap and enhances the optical absorption. However, the defect density increased and the electrical property degrades as the Ge content increased. The hydrogen dilution was found to be an effective approach to improve the material quality [3,4], and we have also demonstrated the effect of hydrogen dilution in our previous work [5].

In the development of a-Si$_{1-x}$Ge$_x$:H solar cells, the bandgap discontinuity between the undoped a-Si$_{1-x}$Ge$_x$:H and doped a-Si:H layers creates a potential barrier and accumulates considerable defects near the interfaces. The charged defects influence on the electric field distribution and lead to the decrease in V$_{OC}$ and FF. Yang et al. have proposed that the graded bandgap absorber can modify the electric field distribution and improve the cell efficiency since the profile of charged defect depends on the design of the bandgap grading [6]. Several groups have investigated the appropriate bandgap grading structure of the

absorber numerically and the results were also well matched with the experimental results [7–9]. However, there are still possibilities in designing the graded bandgap structure. In this work, we carried out experiments and focused on the relation between the bandgap grading width and the performance of a-Si$_{1-x}$Ge$_x$:H single-junction solar cells.

2. Experiment

The deposition was conducted in a single chamber system composed of a load-lock, a transfer and a deposition chamber. It was a 27.12 MHz radio-frequency plasma-enhanced chemical vapor deposition (PECVD) system with a gas mixture of SiH$_4$, GeH$_4$, B$_2$H$_6$, PH$_3$ and H$_2$. The a-Si$_{1-x}$Ge$_x$:H undoped layer was deposited on the corning eagle 2000 glass substrate for the measurement of the optical property. The a-Si$_{1-x}$Ge$_x$:H single-junction solar cells were deposited on the SnO$_2$:F coated glass substrates in a superstrate configuration. The bandgap grading layer was achieved by continuously varying the germane-to-silane flow rate ratio during the deposition process. After the deposition, the cells were transferred to a sputter chamber to deposit the TCO/Ag back contacts.

The deposited thin-films were measured by UV/VIS spectroscopy to obtain their optical transmittance. The bandgaps were obtained by analyzing the transmittance spectra using Tauc's method [10]. The film Ge content (x = Ge/(Si + Ge)) was estimated by the X-ray photoelectron spectroscopy (XPS) with pre-cleans before each measurement. The J-V characteristics of a-Si$_{1-x}$Ge$_x$:H single-junction solar cells were measured under AM1.5 G illumination. The experimental error of J-V results was within 3%.

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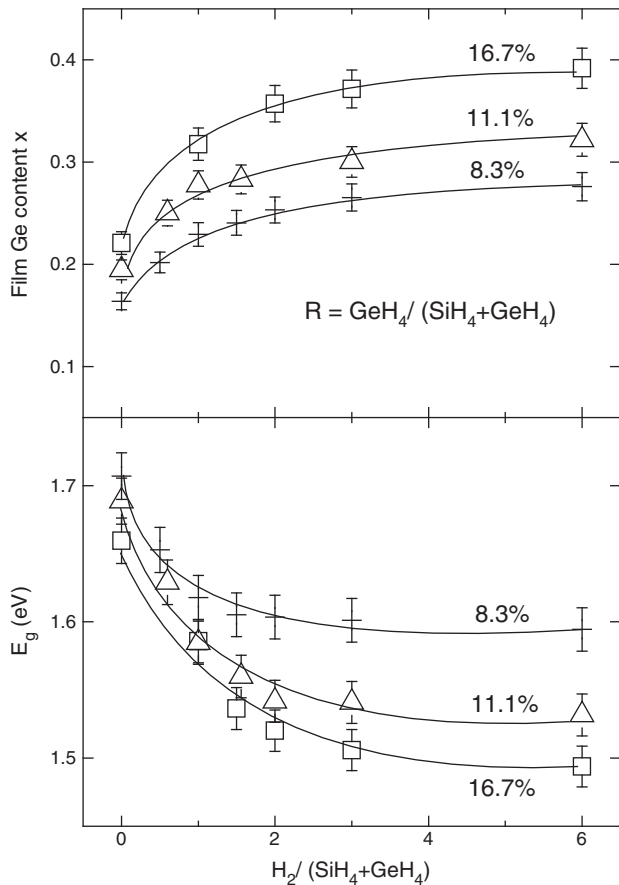   E-mail address: bear0300022@gmail.com (H.-J. Hsu).

Fig. 1. The dependence of H_2 dilution ratio $(H_2/(SiH_4 + GeH_4))$ on the film Ge content and E_g as a function of R. The cross, triangle and square symbols correspond to the samples with R = 8.3%, 11.1% and 16.7%, respectively. The lines were drawn to guide the eye.

3. Results

3.1. Effect of H_2 dilution on the film Ge content and bandgap

Fig. 1 demonstrates the dependence of H_2 dilution ratio $(H_2/(SiH_4 + GeH_4))$ on film Ge content and bandgap with different GeH_4 gas flow ratio (R). As the H_2 dilution ratio increased from 0 to 6, the film Ge content increased significantly for each R. The film Ge content changed more rapidly in the low-H_2-dilution region from 0 to 3. With further increase in the H_2 dilution ratio, the film Ge content varied slightly and seemed to reach saturation. Moreover, as the R increased from 8.3 to 16.7%, the film Ge content further increased. Similarly, the bandgap decreased as the H_2 dilution ratio increased since more Ge incorporated into the film. In fact, hydrogen dilution influenced the film property in a more complicated way which was beyond the scope of this work, where

we simply demonstrated some results related to the bandgap. As a result, by adjusting the H_2 dilution ratio and R, the bandgap can be tuned from 1.70 to 1.50 eV.

3.2. The effect of bandgap grading width on the performance of a-$Si_{1-x}Ge_x$:H single-junction solar cells

Fig. 2(a) and (b) illustrates the schematic band structure of a-$Si_{1-x}Ge_x$:H single-junction solar cells without and with bandgap grading layers at the p/i and the i/n interfaces. The valence and the conduction bands were assumed to shift equally as the film Ge content was varied in the bandgap grading layer. The lowest bandgap of a-$Si_{1-x}Ge_x$:H absorber was 1.55 eV which corresponded to the Ge content of 35%, while the a-Si:H doped layers had a bandgap of approximately 1.75 eV. The p/i and the i/n grading regions consisted of three layers having identical thickness. The Ge contents in the above mentioned layers were 20, 26 and 31%. The layers with specific Ge contents were employed in all the cells presented in this work. To investigate the appropriate bandgap grading structure, the p/i grading width was varied from 0 to 30 nm and the i/n grading width was varied from 0 to 120 nm. The total thickness of a-$Si_{1-x}Ge_x$:H was fixed at 230 nm for every cell presented.

Fig. 3 shows the J-V characteristics of a-$Si_{1-x}Ge_x$:H single-junction solar cells with different i/n grading width. The total absorber thickness is 230 nm for all the cell. The increase in the i/n grading width is accompanied by the decrease in the thickness of the lowest bandgap material. As the i/n grading increased from 0 to 120 nm, the V_{OC} and FF increased to 0.80 V and 71.42%, respectively. However, the J_{SC} also dropped to 14.17 mA/cm^2 as the i/n grading width reached 120 nm. The drop in J_{SC} limited the cell efficiency and the i/n grading width was optimized as the 45 nm. On the other hand, the J-V characteristics of a-$Si_{1-x}Ge_x$:H single-junction solar cells with different p/i and i/n grading width were investigated and demonstrated in Fig. 4. The absorber thickness was fixed at 200 nm for this series of cells. As the p/i grading width increased from 0 to 20 nm, the V_{OC} and FF were improved to 0.75 V and 69.57%, respectively. Only a slight difference in J_{SC} was observed. However, after further elongating in the p/i grading width, the J_{SC} and FF dropped significantly. The cell has higher efficiency as the p/i grading width was 20 nm.

4. Discussion

4.1. Effect of H_2 dilution on the film Ge content and bandgap

As can be seen from Fig. 1, the increase in H_2 dilution ratio increased the film Ge content in different R. The mechanism of H_2 on film Ge content is still not well understood. One possibility is that H_2 may shift the gas phase reaction from the formation of dihydride/polyhydride precursors to the formation of trihydride precursors [11]. The GeH_3 precursors had longer lifetime at the growing surface which enabled them to bond in the lower free energy sites. Moreover, as the H_2 dilution increased, the atomic hydrogen at the growing surface also increased. The abundant atomic hydrogen
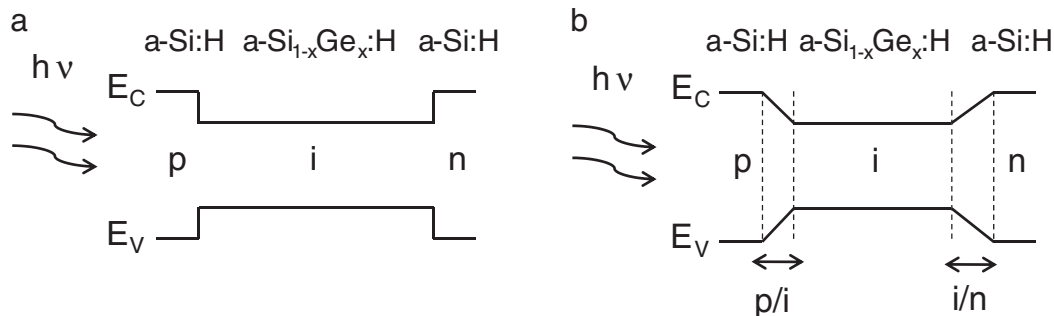

Fig. 2. The schematic band structure of the a-$Si_{1-x}Ge_x$:H single-junction cell (a) without bandgap grading, or (b) with bandgap grading at both the p/i and the i/n interfaces.
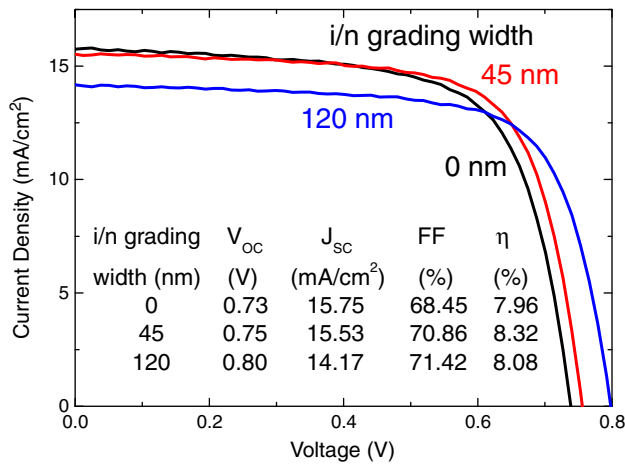
Fig. 3. The J-V characteristics of a-Si$_{1-x}$Ge$_x$:H single-junction solar cells as a function of i/n grading width under AM1.5 G illumination. The total absorber thickness was fixed at 230 nm for all the cells.

enhanced the surface mobility of the precursors and induced etching effect which selectively etched the undesirable bonding as observed from the reduction in deposition rate [12]. The smaller deposition rate also assisted the atomic relaxation [11]. As a result, the bonding of Ge related species might be strengthened which resulted in a better resistance to the H etching, thereby increased the film Ge content. Since the bandgap is the weighted average of every bonding in the film, the increase in film Ge content resulted in the reduction in bandgap.

4.2. The effect of bandgap grading width on the performance of a-Si$_{1-x}$Ge$_x$:H single-junction solar cells

As can be seen in Fig. 3, the V$_{OC}$ increased as the i/n grading width elongated. The cell without the i/n grading may contain considerable defects at the interfaces. These interface defects may trap and accumulated charged carriers. The accumulation of charged defects strengthened the electric field near the interfaces whereas weakening the electric field in the bulk material [8,9]. As a result, the bulk recombination rate and dark leakage current increased. Moreover, the accumulated charged defects can also act as an opposite force against the build-in electric field. Both factors led to the reduction in V$_{OC}$. By employing the bandgap grading, the distribution of charged defects can be properly controlled. Therefore, the electric field can be smoother and more
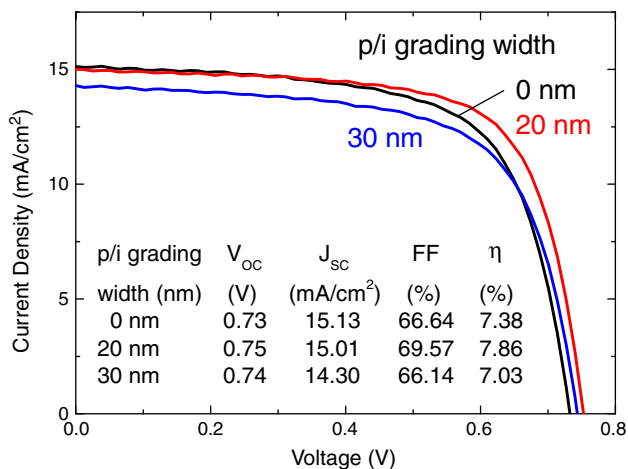

Fig. 4. The J-V characteristics of a-Si$_{1-x}$Ge$_x$:H single-junction solar cells as a function of p/i grading width under AM1.5 G illumination. The total absorber thickness was fixed at 200 nm for all the cells.

Table 1
The J-V characteristics of a-Si$_{1-x}$Ge$_x$:H single-junction solar cells with different bandgap grading structures. The total absorber thickness was the same for each cell.

	V$_{OC}$ (V)	J$_{SC}$ (mA/cm^2)	FF (%)	η (%)
Without grading	0.68 ± 0.003	15.07 ± 0.12	61.16 ± 1.44	6.31 ± 0.17
20 nm p/i + 45 nm i/n	0.75 ± 0.001	15.51 ± 0.03	70.56 ± 0.33	8.27 ± 0.03
Optimized doped layers and bandgap grading	0.75 ± 0.002	16.31 ± 0.20	70.38 ± 0.39	8.59 ± 0.08

uniform throughout the absorber layer which reduced the recombination rate and therefore increased the V$_{OC}$.

As shown in Fig. 3, the shunt resistance slightly increased which may imply that the leakage current was reduced. The FF was benefited from the improved electric field since the distorted electric field distribution was detrimental to the carrier transport and extraction. Furthermore, the potential gradient established by the i/n grading may facilitate the hole transport [6]. Since the low drift mobility of hole in amorphous material, the hole transport was generally recognized as the limiting factor of the carrier extraction efficiency and FF. Therefore, as the i/n grading width increased from 0 to 120 nm, the FF increased which may be due to both the better electric field distribution and facilitation of the hole transport. However, the J$_{SC}$ decreased as the i/n grading increased. The reduction in J$_{SC}$ was due to the loss in the absorption of low-energy photons since the thickness of lowest bandgap material shrunk as the i/n grading width increased. Considering the decrease in J$_{SC}$, the cell efficiency was optimized as the i/n grading width was 45 nm.

On the other hand, the V$_{OC}$ and FF increased as the p/i grading increased from 0 to 20 nm. The trend is similar to the i/n grading series and can be attributed to the improved electric field distribution. However the potential gradient established by the p/i grading would hinder the hole transport. The deteriorated hole transport dominated as the p/i grading width exceeded 20 nm and accounted for the decrease in FF and J$_{SC}$. The difficulty of hole transport through the potentially unfavorable p/i grading might constrain the p/i grading width below 20 nm. Table 1 compares the a-Si$_{1-x}$Ge$_x$:H single-junction solar cells with different grading structure. As shown in Table 1, the bandgap grading indeed played an important role to the improvement in cell efficiency. Together with a thinner n-type doped layer, 20 nm p/i grading width and 80 nm i/n grading width, cell efficiency of 8.59% has been achieved.

5. Conclusion

We have found that the hydrogen dilution is strongly related to the film Ge content and both the p/i and the i/n grading were effective in increasing the cell efficiency. The elongation in the i/n grading width enhanced the V$_{OC}$ and FF. The increase in the shunt resistance suggested that the reduction in the leakage current which increased the FF. However, the J$_{SC}$ was also reduced because of the loss in absorption of low-energy photons. On the other hand, similar trend was observed as the p/i grading width increased from 0 to 20 nm. Further increase in the p/i grading width deteriorated the FF and J$_{SC}$. Presumably the hole transport was deteriorated by the p/i grading. Combining the effect of bandgap grading on the V$_{OC}$, J$_{SC}$ and FF, the suitable thicknesses of the p/i and the i/n grading width were 20 nm and 45 nm, respectively. Further optimization of the thickness of the n-type doped layer in conjunction with a 20 nm p/i and 80 nm i/n grading width obtained an a-Si$_{1-x}$Ge$_x$:H single-junction cell with η = 8.59%, V$_{OC}$ = 0.75 V, J$_{SC}$ = 16.31 mA/cm^2 and FF = 70.38%.

Acknowledgement

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