ELSEVIER Solar Energy Materials and Solar Cells 34 (1994) 303-312

Solar Energy Materials and Solar Cells

Effects of the i-layer properties and impurity on the performance of a-Si solar cells

Yoshihiro Hishikawa *, Masao Isomura, Shingo Okamoto, Haruhisa Hashimoto, Shinya Tsuda

Functional Materials Research Center, SANYO Electric Co., Ltd., 1-18-13 Hashiridani, Hirakata, Osaka 573, Japan

Abstract

The relation between the opto-electric properties of an a-Si:H i-layer and the performance of a-Si solar cells are extensively investigated, paying careful attention to the controllable range of the opto-electric properties and the effects of the impurities. It is shown that even trace amounts (10^{19} cm^{-3} or less) of oxygen impurity in the i-layer affect the film properties and the solar cell performance. When the impurity concentration and other undesirable factors are suppressed, the mutual relationship among the i-layer properties becomes clear. Although there is a limitation in the controllable range of the properties of device-quality a-Si:H, techniques such as a hydrogen plasma treatment can improve the controllable range. Guidelines to design and optimize the i-layer for solar cells are discussed on the basis of these experimental results. A total-area conversion efficiency of 12.0% is achieved for a 10 cm × 10 cm integrated a-Si solar cell submodule.

1. Introduction

The conversion efficiency of optimized amorphous silicon (a-Si) solar cells has recently been improved to the level of about 13% for small area cells [1-3]. Many materials, such as the p-layer, i-layer, n-layer, interface layer, transparent electrode, and back electrode, contribute to the improvement of this efficiency Among these, the i (intrinsic) layer, which works as the photovoltaic layer, plays the decisive role in solar cell performance. Although the i-layer may appear to reach a certain level of optimization, many factors actually remain to be revealed. Here,

---

* Corresponding author.

SSDI 0927-0248(94)00046-U

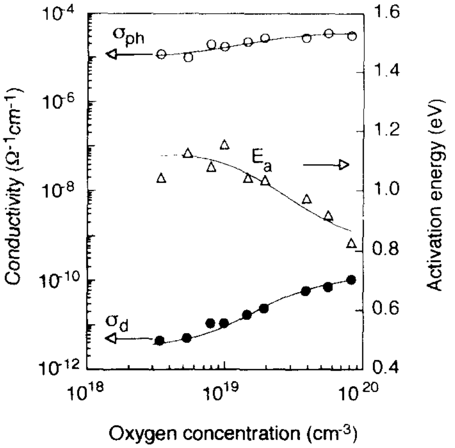


Fig. 1. σ_{ph}, σ_d, and E_a of intrinsic a-Si:H films as functions of the oxygen concentration. The oxygen concentration is controlled by adding CO_2 to the material gas (SiH_4). Other deposition conditions are the same as those for typical high-efficiency solar cells. Lines are drawn for visual aid.

the results of recent studies on a-Si:H i-layers are discussed in regard to their effects on solar cell performance. The next targets for further improvement are also investigated.

2. Effects of impurities in the i-layer

Impurities such as oxygen, carbon, and nitrogen are included even in a device-quality a-Si i-layer, and when these impurities reach the order of $\sim 10^{20}$ cm^{-3}, they increase the defect density, damage solar cell performance, and enhance the light-induced instability of a-Si [4–6]. However, the effects of these impurities in lower concentration levels are not well understood. Fig. 1 shows the photoconductivity (σ_{ph}), dark conductivity (σ_d), and activation energy of σ_d (E_a) of intrinsic aSi:H films as functions of the oxygen concentration (C_o). σ_{ph} and σ_d increase, and E_a decreases as C_o increases, although their changes are small when $C_o < 10^{19}$ cm^{-3}. Similarly, the conversion efficiency of a typical single junction a-Si solar cell (thickness of i-layer: 2700–6700 Å) slightly decreases when C_o is $\sim 10^{19}$ cm^{-3}, and then decreases to 8.2% when $C_o = 9 \times 10^{20}$ cm^{-3} (Fig. 2). The drop in the conversion efficiency is mainly due to the drop in the fill factor (FF). The short-circuit current (I_{sc}) and the open-circuit voltage (V_{oc}) are not much affected by oxygen incorporation. These results clarify the fact that it is essential to suppress the impurities such as oxygen in order to improve the performance of a-Si solar cells, even when $C_o \sim 10^{19}$ cm^{-3} or less. The results of Figs. 1 and 2 also suggest that the origin of the effects of the oxygen impurity is not only the defects (dangling bond, etc.) induced by oxygen, but also the shift in the Fermi level as evidenced by the significant change in E_a.

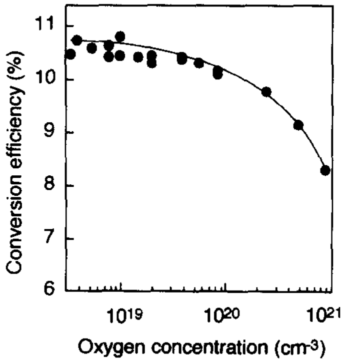


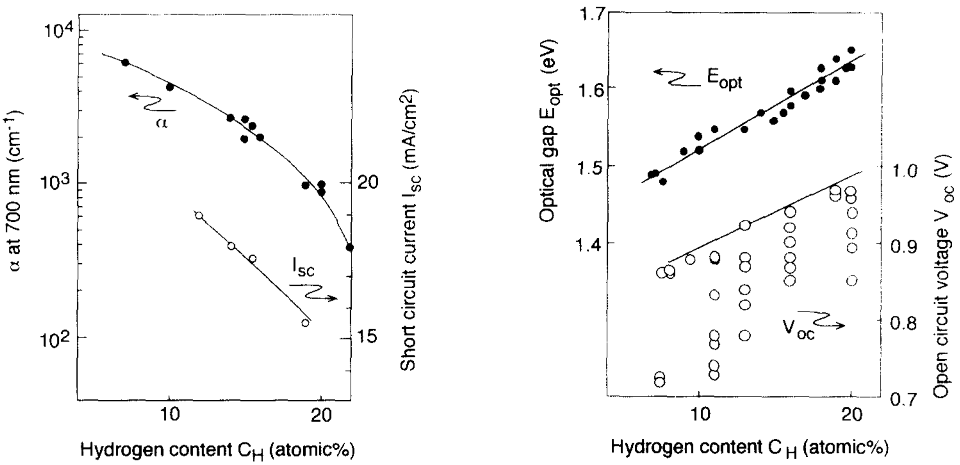
Fig. 2. The conversion efficiency of a-Si solar cells as a function of the oxygen concentration. The oxygen concentration is controlled by adding CO_2 to the material gas (SiH_4). The thickness of the i-layer is 2700–6700 Å. Other deviced parameters, such as the transparent electrode and the thickness of doped layers, are identical for all samples, and not optimized for high efficiency. The line is drawn for visual aid.

It is noted that the conversion efficiency of solar cells decreases and σ_{ph} increases as C_0 increases. Therefore, a high σ_{ph} does not mean a "high-quality" a-Si i-layer for solar cells when the i-layer contains impurities. It should also be noted that E_a exceeds 1 eV when C_o is $< 10^{19}$ cm^{-3}, which shows that the "intrinsic" E_a of device-quality a-Si : H (hydrogen content ~ 15 atomic%) exceeds 1 eV, and a smaller E_a is an indication of impurities.

3. Optimization of i-layer properties

3.1. *Trade-off among the properties of the i-layer*

The conversion efficiency of a solar cell is the product of V_{oc}, I_{sc}, and FF. It is well known that V_{oc}, I_{sc}, and FF are principally related to the bandgap, optical absorption coefficient (α), and defect density (N_d) of the i-layer. However, it is not easy to custom design the i-layer, because a trade-off exists among its properties. For example, a high α, especially at the wavelength of 700–800 nm, is required in order to improve I_{sc} (Fig. 3a). As α increases as the bandgap decreases, a narrow bandgap is preferred to improve I_{sc}. On the other hand, the bandgap should be wide in order to attain a high V_{oc} (Fig. 3b). In this study, E_{opt} is determined from the $(\alpha h\nu)^{1/3}$ versus $h\nu$ plots instead of the Tauc's plot (or $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot), in order to discuss small change (~ 0.2 eV) in α. The value of E_{opt} determined from the Tauc's plot is usually larger than that determined from the $(\alpha h\nu)^{1/3}$ plot by 0.1–0.2 eV, and has ambiguity due to poor linearity of the $(\alpha h\nu)^{1/2}$ plot [7]. A similar trade-off between V_{oc} and I_{sc} always occurs in regard to the bandgap of the i-layer. Therefore, the most important task in optimizing the



(a) (b)

Fig. 3. (a) α at 700 nm of intrinsic a-Si:H films and I_{sc} of a-Si solar cells, and (b) E_{opt} of intrinsic a-Si:H films and V_{oc} of a-Si solar cells as functions of the hydrogen content C_H of the i-layers. E_{opt} is determined from the $(\alpha h\nu)^{1/3}$ versus $h\nu$ plots. Device structures, such as the thickness of the i-layer (~ 5000 Å), are identical for the solar cells in (a). As those structures are not unified for the solar cells in (b), V_{oc} scatters. However, the upper limit of V_{oc} correlates well with C_H. Lines are drawn for visual aid.

i-layer is to understand the relation of its properties and deposition conditions, and the controllable range of the properties as a whole.

3.2. Controllable range of the i-layer

Extensive research has been conducted into optimizing intrinsic a-Si:H for solar cells deposited by plasma-CVD. It is empirically accepted that conditions for a conventional "device-quality" a-Si:H i-layer include the suppression of impurities, a relatively low RF power (well below 100 mW/cm^2), a moderate gas pressure of 13–40 Pa (0.1–0.3 Torr), the use of 100% SiH_4 or SiH_4 lightly balanced with H_2 as the material gas, the suppression of gas-phase polymerization in the plasma, no ion bombardment or a mild ion bombardment, and a substrate temperature (T_s) of 150–250°C [8–10]. Recently, a rather simple relationship among the properties of intrinsic a-Si:H, deposited under these conditions, has been found. That is, the optical, electrical, and structural properties of a-Si:H are mainly determined by T_s and the film deposition rate (R_d). Furthermore, there is almost a one-to-one relationship among these properties, which becomes clear when the impurities, polymerization, or powder formation in the plasma, and the ion bombardment are suppressed [8]. This has made it clear that the trade-off is actually inevitable as long as the conventional "device-quality" deposition conditions are used. However, it has also made a unified discussion of their mutual relationship and optimization easier than before. Among these, the relationship

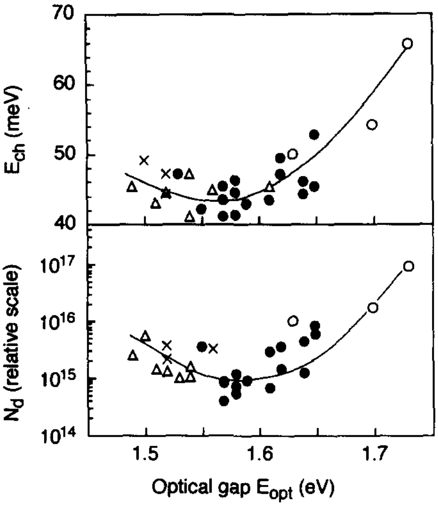


Fig. 4. Defect density (N_d) and slope of the Urbach tail (E_{ch}) of a-Si:H as functions of the optical gap (E_{opt}). N_d and E_{ch} are calculated from the constant photocurrent method. E_{opt} is determined from the $(\alpha h\nu)^{1/3}$ versus $h\nu$ plots. ○, ●, ×, and △ indicate that T_s is about 100, 150, 250, and 400°C, respectively. Lines are drawn for visual aid.

between N_d and other properties are not well understood. Fig. 4 shows N_d and the slope of the Urbach tail (E_{ch}) of a-Si:H as a function of the optical gap, calculated from α spectra measured by CPM (Constant Photocurrent Method). Considering that the different symbols correspond to different T_s, the results of Fig. 4 suggest that N_d and E_{ch} are also mainly dependent on the optical gap rather than on individual deposition conditions such as T_s, like many other optoelectric properties of a-Si:H. The scatter in the experimental data is probably due to the fact that CPM measurements are sensitive to experimental details. Both N_d and E_{ch} have broad minima at E_{opt} 1.55–1.61 eV. The E_{opt} of optimized i-layers for a-Si solar cells usually falls within this range.

3.3. I-layer properties and solar cell structures

The optimum structure of a-Si solar cells and the optimum i-layer properties are significantly dependent on each other. For example, Fig. 5 shows the performance of a-Si solar cells with two kinds of i-layers as functions of the i-layer thickness. One i-layer (denoted by ●) has $E_{opt} = 1.56$ eV, α at 700 nm = 2500 cm^{-1} and $N_d \sim 1 \times 10^{15}$ cm^{-3}, and the other (denoted by ○) has $E_{opt} = 1.65$ eV, α at 700 nm = 800 cm^{-1}, and $N_d \sim 1 \times 10^{16}$ cm^{-3}. Device parameters other than the i-layer are identical for all the samples. V_{oc} is nearly constant over the range of i-layer thickness in this study, and reflects the value of E_{opt}. I_{sc} also reflects α well. FF reflects N_d when $d \geqslant 5000$ Å, and saturates for a thinner d. As a result, the optimum i-layer thicknesses are ~ 2000 Å for a 1.65 eV i-layer, and ~ 8000 Å for a 1.56 eV i-layer. This result also indicates that the conversion efficiency is readily

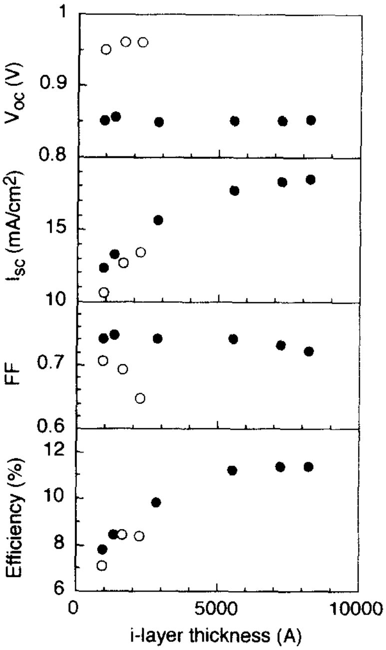


Fig. 5. Performance of a-Si solar cells as functions of the i-layer thickness. One i-layer (denoted by ●) has $E_{opt} = 1.56$ eV, α at 700 nm = 2500 cm^{-1} and $N_d \sim 1\times10^{15}$ cm^{-3}, and the other (denoted by ○) has $E_{opt} = 1.65$ eV, α at 700 nm = 800 cm^{-1}, and $N_d \sim 10^{16}$ cm^{-3}. Device parameters other than the i-layer are identical for all the samples, and not optimized for high efficiency.

improved if N_d is successfully reduced while conserving E_{opt}, which will be discussed later.

4. Further improvement in i-layer properties

The controllable range and the mutual relationship of a-Si : H films are limited, as discussed in the previous chapter. However, recent studies have also revealed that it is not a limitation of the a-Si material itself, but a limitation of the conventional "optimized" deposition conditions of plasma-CVD for device-quality a-Si : H. The following two possibilities exist for further improving the i-layer for a-Si solar cells.

4.1. Optimization of conventional plasma-CVD

In conventional plasma-CVD, the performance of solar cells is usually damaged for $T_s > 250$°C, although the properties of the a-Si film are good. This is mainly due to the fact that a high T_s increases damage to underlying layers, such as the p-layer, during deposition of the i-layer of the solar cell [11]. It has recently been

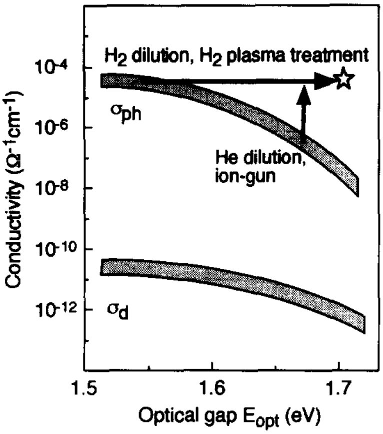


Fig. 6. Schematic diagram of σ_{ph} and σ_d of intrinsic a-Si:H films as functions of E_{opt}, determined from the $(\alpha h\nu)^{1/3}$ versus $h\nu$ plots. Shaded areas indicate the range where data from films deposited under conventional device-quality conditions exists. The solid arrow shows the effect of strong hydrogen dilution of hydrogen plasma treatment on σ_{ph}. The dotted arrow shows the effect of strong helium dilution or ion-gun CVD. The star indicates the property of a film fabricated by a repetition of deposition and the hydrogen-plasma treatment.

reported that narrow-gap i-layers can be deposited at reduced T_s by heating SiH_4 gas in the conventional plasma-CVD method [12]. This can contribute to the improvement of solar cell performance by reducing the damage. Heating the mesh electrode in a triode plasma CVD apparatus (DREP) [13] may also improve the performance of a-Si solar cells by reducing the N_d at high R_d.

4.2. Improving the properties of the i-layer beyond conventional limitations

Techniques such as hydrogen plasma treatment, strong hydrogen or helium dilution of the material gas, and an ion-gun CVD can be used to fabricate a device-quality a-Si:H i-layer with a wide bandgap which cannot be achieved by conventional deposition conditions [14]. The shaded areas of Fig. 6 show the σ_{ph} and σ_d of conventional device-quality intrinsic a-Si:H films as functions of E_{opt}. As indicated by the arrows in the figure, these techniques can result in a wide a-Si:H with $E_{opt} \sim 1.7$ eV while conserving high σ_{ph}. The I–V curves of a-Si solar cells with conventional optimized i-layers and a hydrogen-plasma treated i-layer are shown in Fig. 7. This is a typical example of the controllable range of solar cell performance related to the i-layer. The high $V_{oc} > IV$ and good FF > 0.7 confirms the wide bandgap and low N_d. As for narrow gap a-Si:H, techniques to fabricate better i-layers than conventional methods have not been successful so far, as far as solar cell performance is concerned. However, the results of film properties for the chemical annealing method [15], catalytic [16] or hot-wire CVD [17], and photo-CVD [18] are encouraging because they show the possibility that the controllable

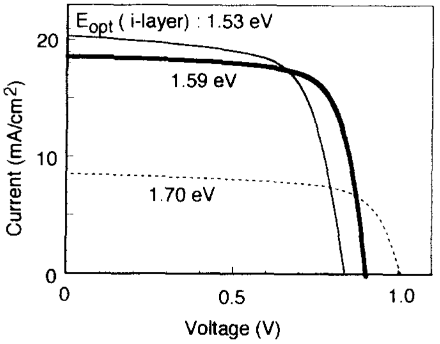
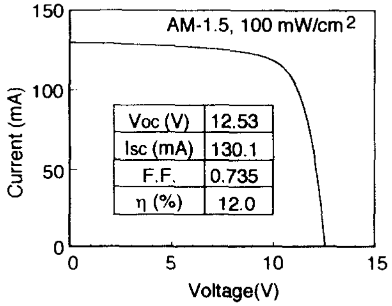


Fig. 7. Current–voltage characteristics of single-junction a-Si solar cells with various i-layers. The thin solid line, thick solid line, and dotted line correspond to the solar cells whose E_{opt} of the i-layer are 1.53, 1.59, and 1.70 eV, respectively. The 1.70 eV i-layer is fabricated by using the hydrogen-plasma treatment technique (Star in Fig. 6).

range of the a-Si properties can be significantly improved by altering precursors for the i-layer deposition.

5. High-efficiency a-Si solar cell submodule

By combining optimization of conventional high-quality i-layer and other technologies, such as the hydrogen-plasma treated wide-gap buffer layer at the p-i interface, a total-area conversion efficiency of 12.0% for a 10 cm × 10 cm integrated submodule has been achieved (Fig. 8).



Voc (V)	12.53
Isc (mA)	130.1
F.F.	0.735
η (%)	12.0

Fig. 8. Illuminated $I-V$ characteristics of an integrated-type single-junction a-Si solar cell submodule of 10×10 cm^2, measured at JMI.

6. Summary

The optical and electrical properties of the a-Si:H i-layer are of prime importance in the performance of a-Si solar cells. Recent studies have shown the following important facts concerning the relation between the i-layer properties and solar cell performance and their improvements.

(1) Oxygen impurities in the i-layer affect the film properties and solar cell performance even at low concentrations of $\sim 10^{19}$ cm^{-3} or less. The photoconductivity and dark conductivity increase, and the conversion efficiency decreases as the oxygen concentration increases. Therefore, it is essential to suppress impurities in order to improve the performance of a-Si solar cells.

(2) The midgap defect density and the slope of the Urbach tail of intrinsic a-Si:H film, as measured by the constant photocurrent method, are mainly dependent only on the optical gap just like other properties of the films, and are minimal when the optical gap, determined from the $(\alpha h\nu)^{1/3}$ versus $h\nu$ plot, is 1.55–1.61 eV. These films improve the fill factor and the conversion efficiency of the solar cells when used as the i-layer.

(3) Although the controllable range of the i-layer properties is limited when conventional "device-quality" deposition conditions are used, techniques such as a strong hydrogen dilution of the material gas, a hydrogen-plasma treatment, or an ion-gun CVD method can further expand the controllable range and improve the open-circuit voltage of the solar cells. New techniques, such as heating the material gas, are also useful for depositing high-quality i-layers at a low substrate temperature. A total-area conversion efficiency of 12.0% is achieved for a 10 cm × 10 cm integrated single-junction a-Si solar cell submodule.

Acknowledgement

This work was supported by NEDO as a part of the New Sunshine Program under the Ministry of International Trade and Industry.

References

[1] Y. Hishikawa et al., Proc. Materials Research Society, Spring Meeting, San Francisco, 1993 (to be published).
[2] S. Okamoto et al., Proc. 11th EC Photovoltaic Solar Energy Conf., Montreux, 1992, p. 537.
[3] J. Yang, R. Ross, T. Glatfelter, R. Mohr and S. Guha, Mater. Res. Soc. Symp. Proc. 258 (1989) 435.
[4] M. Ohnishi, S. Tsuda, T. Takahama, M. Isomura, Y. Nakashima, N. Nakamura, S. Nakano, T. Yazaki and Y. Kuwano, Jpn. J. Appl. Phys. 26 (1987) 1408.
[5] M. Stutzmann, W.B. Jackson and C.C. Tsai, Phys. Rev. B32 (1985) 23.
[6] D.E. Carlson, J. Vac. Sci. Technol. 20 (1982) 290.
[7] Y. Hishikawa et al., Jpn. J. Appl. Phys. 30 (1991) 1008.

[8] Y. Hishikawa, S. Tsuda, K. Wakisaka and Y. Kuwano, J. Appl. Phys. 73 (1993) 4227.
[9] J.P.M. Schmitt, Thin Solid Films 62 (1979) 335.
[10] A. Gallagher, Int. J. Solar Energy 5 (1989) 193.
[11] M. Nishikuni, H. Haku, M. Isomura, S. Okamoto, K. Sayama, T. Takahama, T. Matsuoka, S. Tsuda, S. Nakano, M. Ohnishi and Y. Kuwano, J. Non-Cryst. Solids 114 (1989) 181.
[12] M. Isomura et al., Proc. SPIE's 1993 Int. Symposium on Optical Materials Technology for Energy Efficiency and Solar Energy Conversion, Sandiego, 1993 (to be published).
[13] G. Ganguly and A. Matsuda, Mater. Res. Soc. Symp. Proc. 258 (1992) 39.
[14] Y. Hishikawa, S. Tsuge, N. Nakamura, S. Tsuda, S. Nakano and Y. Kuwano, J. Appl. Phys. 69 (1991) 508.
[15] D. Das, H. Shirai, J. Hanna and I. Shimizu, Jpn. J. Appl. Phys. 30 (1991) L239.
[16] H. Matsumura, J. Appl. Phys. 65 (1989) 4396.
[17] A. Mahan, J. Carapella, B.P. Nelson, R.S. Crandall and I. Belberg, J. Appl. Phys. 69 (1991).
[18] Y. Mishima et al. Jpn. J. Appl. Phys. 22 (1983) L41.