Hydrogenated Amorphous Silicon Germanium Alloys for High Efficiency and Stable Solar Cells

Akira TERAKAWA

April 1999
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Abstract

This work investigates the properties of hydrogenated amorphous silicon germanium (a-SiGe:H) alloys as photovoltaic materials, which are good candidates for use as the bottom photo-absorber of tandem solar cells. a-SiGe:H films were deposited by a plasma-CVD method using SiH$_4$, GeH$_4$, and H$_2$ gas mixtures. The difficulties of a-SiGe:H as ternary alloys due to the intermixing of respective parameters, such as the deposition conditions, compositions, hydrogen bonding structures, optical gap ($E_{\text{opt}}$), electronic properties, solar cell performance and photo-instability, were systematically unraveled. This work provided new insights into a wide variety of aspects, from particular issues related to a-SiGe:H alloys, to the universal issues of a-Si related materials, and from fundamental material properties to device characteristics.

In Chapter 2, the correlations among deposition conditions, compositions and material properties were systematically investigated. $E_{\text{opt}}$ of a-SiGe:H, which is an essential factor in designing photovoltaic material, was quantitatively represented as a function of the hydrogen content ($C_H$) and germanium content ($C_{Ge}$). Furthermore, it was shown that the optimum composition for a certain $E_{\text{opt}}$ ($= 1.32$ eV) exists, and shifts to the lower $C_H$ region after light soaking. $C_H$ and hydrogen bonding configurations were suggested as being important in determining both the initial properties and the photo-instability.

In Chapter 3, the composition dependence of the inhomogeneous hydrogen bonding structures in a-SiGe:H was investigated by means of an infrared (IR) absorption spectroscopy method. It was shown that the structural differences of a-SiGe:H with $C_H$ are mainly caused in the regions around Si atoms. H-Si bonding configurations of the samples deposited from highly-H$_2$-diluted source gas are almost random, while those from low-diluted source gas selectively contain polyhydride bonds. Besides, the coefficient of the preferential hydrogen attachment to Si over to Ge ($P$), which causes inhomogeneity of hydrogen bonding structures, has positive correlations to both $C_H$ and $C_{Ge}$. The $P$ value is considered to be determined not simply by the statistical difference of the bonding probabilities of H to Si and to Ge, but by the kinetics of H elimination during film growth.

In Chapter 4, in order to reveal the effects of i-layer $E_{\text{opt}}$ and the composition of a-SiGe solar cells on stability against light soaking, the light-induced degradation and thermally-induced
recovery behaviors of a-SiGe cells with a constant $E_{\text{opt}}$ and different compositions, and those with various $E_{\text{opt}}$, were systematically investigated. It was suggested that compositional factors such as $C_H$ mainly affect the saturated defect density after intense light soaking ($N_{\text{sat}}$), while $E_{\text{opt}}$ affects the degradation time constant. It was clearly shown that a-SiGe cells with lower $C_H$ and/or Si-H$_2$ content were more stable in a constant $E_{\text{opt}}$ system. This result confirms the contribution of incorporated hydrogen atoms on metastable defect creation. A-SiGe solar cells with a narrower $E_{\text{opt}}$ degrade more slowly than, but recover as fast as, cells with a wider $E_{\text{opt}}$. This is because light-induced processes are suppressed in materials with a narrower $E_{\text{opt}}$, while thermally-induced processes do not depend on $E_{\text{opt}}$. Furthermore, it was proved that $N_{\text{sat}}$ depends on the temperature more strongly for narrower $E_{\text{opt}}$ alloys. Therefore, operating conditions should be considered in the design of highly-efficient solar cell submodules.

In Chapter 5, the knowledge gained in the present study was applied to a-SiGe:H material design for high-efficiency solar cells and modules. The world's highest stabilized efficiency of 3.3% for an a-SiGe single junction solar cell (1 cm$^2$) was achieved under R65 filtered light. Using this a-SiGe cell at the bottom, the world's highest stabilized efficiencies of 10.6% for an a-Si/a-SiGe tandem cell (1 cm$^2$) was also achieved. Furthermore, the world's highest stabilized efficiencies of 9.5% for an a-Si/a-SiGe superstrate submodule (30$\times$40 cm$^2$) was achieved by combining the cell design technique with some other technologies.

Finally in Chapter 6, the conclusions of the present work were summarized together with suggestions for future work.
Acknowledgments

The author wishes to express his sincere gratitude to Professor Hiroyuki Matsunami of Kyoto University for his continuous guidance and for helpful suggestions throughout Ph.D course and for this thesis.

The author is also grateful to Professor Shigeo Fujita and Professor Kunihide Tachibana of Kyoto University for their guidance and suggestions during the preparation of this thesis.

Sincere appreciation is extended to Professor Hajime Yamashina of Kyoto University for his recommendation and support upon the author's applying for admission to the Graduate School of Kyoto University.

This work was done at the New Materials Research Center of Sanyo Electric Co., Ltd., and was in part supported by the New Energy and Industrial Technology Development Organization (NEDO) as a part of the New Sunshine Program under the Ministry of International Trade and Industry.

The author would like to express a special thank to Dr. Yukinori Kuwano, the president of Sanyo Semiconductor Company (the ex-executive director of the R&D Headquarters of Sanyo) and Dr. Fusao Terada, the present executive director of the R&D Headquarters, for their immeasurable and valuable support. He also wishes to express his great appreciation to Dr. Shoichii Nakano, the general manager of the General Management Planning Office of the R&D Headquarters (the ex-general manager of the New Materials Research Center), Dr. Osamu Ota, the present general manager of the New Materials Research Center, and Dr. Masato Osumi, the general manager of Sanyo Home Appliance Company (the ex-general manager of the Mechatronics Research Center), for their continuous support and encouragement.

The author is also indebted to Dr. Shinya Tsuda, the deputy general manager of the New Battery Division of Sanyo and concurrently the president of Solec Co. Ltd, (the ex-senior manager of the New Electronic Materials Department of the New Materials Research Center) for his guidance, critical reading of technical papers and helpful discussions. He is also grateful to Dr. Seiichi Kiyama, the senior manager of the PV Group of the New Electronic Materials Department of the New Materials Research Center, Dr. Hisaki Tarui, Dr. Makoto Tanaka and Dr. Kenichiro Wakisaka, the managers of the PV Group, for their helpful guidance and continuous encouragement.

The author would also like to thank to the following people at Sanyo:

Tsuyoshi Takahama and Dr. Masato Nishikuni for their kind tutorial guidance when the author
started his research activities in the field of amorphous silicon solar cells in Sanyo.

Katsunobu Sayama and Masaki Shima for their helpful cooperation in the experiments of thin film deposition processes, their analysis sequences of materials and devices, and for fruitful technical discussions.

Akiko Tabata, Mio Saito, Akira Mikami, Shigeki Matsuda and Hiroshi Nonoue, the members of the Materials Characterization Laboratory, for their experimental assistance and advice in the composition analysis of alloy materials by SIMS, XPS and FT-IR measurements.

Dr. Yoshihiro Hishikawa for his fruitful discussions and valuable comments particularly on the construction of kinetic model for hydrogen bonding configurations.

Dr. Masao Isomura and Dr. Shingo Okamoto for their critical reading of some of the technical articles, discussions and useful comments.

Ritsuyo Ikemoto for her assistance in preparing some figures and editing the manuscript, and for her friendship.

Norihiro Terada and Shigeo Yata for following him in Sanyo during his Ph.D course.

Dr. Hisao Haku, Kunimoto Ninomiya, Dr. Eiji Maruyama, Yukihiro Yoshimine and Toshihiro Kinoshita for their helpful assistance and discussions, and all other research members working on amorphous silicon solar cells for their support in so many ways.

And the author finally thanks to his family: his sister and brother-in-law Nobuko and Dr. Mark Buonanno, his parents Katsuko and Makoto Terakawa, and his grandmother Masago Terakawa for their material and moral support and continuous encouragement.
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6.4 Applications to efficient and stable solar cells

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List of Publications

Biographical Note
Chapter 1
Introduction

1.1 Historical background of solar cells

It was 1954 when the first solar cell was invented by Pearson et al. in the Bell Laboratory of AT&T in the USA.\(^1\) Solar cells are energy conversion devices that apply the photovoltaic effect of the p-n junction of semiconductors, and which can cleanly produce electric power from inexhaustible sunlight without any waste. Due to these features, solar cells are expected to be used as a renewable energy source in the next generation, taking the place of fossil fuels such as coal and oil. Since the oil shock in 1973, the research and development of solar cell technologies for practical large-scale photovoltaic use has been accelerated in national projects in many countries and regions including Japan, the USA and Europe. In recent years, solar cells have attracted considerable attention as a solution to increasing serious environmental problems such as the greenhouse effect which causes global warming, the destruction of forests by acid rain and the ultraviolet rays that penetrate the ozone hole. The production volume of solar cells is drastically increasing year by year around the world.\(^2,3\) The Japanese government started a financial support program in 1994 to accelerate the spread of solar power generation systems for private houses and buildings, and is planning to install 5000 MW systems by 2010.

At present, solar cells are expensive compared to commercial electricity generated by thermal or nuclear power plants. Further reduction of the production cost is necessary in order to achieve the spontaneous spread without financial support. The most widely used semiconductor materials for solar cells are single- and poly-crystalline silicon (c-Si and poly-Si), which shared more than 80% of the world's shipment of cells and modules in 1997.\(^3\) The cost limiting factor of c-Si and poly-Si solar cells is 200-400 \(\mu\)m thick Si substrate wafers, which are fabricated through complex and high-temperature processes. Hydrogenated amorphous silicon (a-Si:H) is a good candidate for large-scale and low-cost devices in place of Si wafers. The use of a-Si:H for solar cells made it possible to reduce the thickness of semiconductor layers to less than 0.5 \(\mu\)m. This is because a-Si:H is a direct transition semiconductor and has a remarkably larger absorption coefficient against visible
light than crystalline Si, which is an indirect transition semiconductor. This is a great advantage from the point of view of the material cost.

1.2 Progress in a-Si solar cell technology

a-Si:H was first made in 1969 by Chittick et al. in the UK, using a glow discharge with SiH$_4$ gas. However, in those days, it was believed that amorphous materials were insensitive against doping due to the lack of periodicity of atomic arrangement and were not feasible for junction devices. A breakthrough was reported in 1975 by Spear and LeComber of Dundee University in the UK. They succeeded in substitutional p-type and n-type doping by adding B$_2$H$_6$ and PH$_3$ to source SiH$_4$ gas. The significance of their observations was widely acknowledged, and a-Si:H has received considerable attention as a new electronic material.

The research of a-Si solar cells was started by Carlson and Wronski of RCA in 1976. They initially reported a conversion efficiency of 2.4 % by adopting a p-i-n junction structure. They also reported a conversion efficiency of 5.5 % with a Schottky junction structure. In 1978, an improved efficiency of 4.5 % for a p-i-n junction cell was reported by Hamakawa et al. of Osaka University. In 1979, Kuwano et al. of Sanyo developed two key technologies in this field; one is an "integrated type structure," and the other is a "consecutive, separated chamber reaction method." The concept of the integrated type structure is to connect multiple cells in series on a single substrate in order to generate high output voltage. While, the consecutive, separated chamber reaction method achieved a drastic reduction of impurities in the a-Si:H i-layer contaminated by the source gas intermixing during film deposition. Based on these technologies, Sanyo marketed the first devices — hand-held calculators — powered by a-Si solar cells in 1980. Since then, subsequent research resulted in numerous technologies, such as the minimized optical loss by a-SiC:H window layers, a reduction of the intermixing of impurities by the ultra-high-vacuum (UHV) deposition system, and fabrication of integrated-type structures by the laser patterning method. By the use of these techniques, the conversion efficiency of a-Si solar cells has been improved year by year. The world's highest initial efficiencies of 12.7 % for a p-i-n single-junction cell (1 cm$^2$) and of 12.0 % for a submodule (100 cm$^2$) were achieved by Sanyo in
1.3 Importance of a-SiGe:H alloys for solar cells

For large-scale power generation utilizing a-Si solar cells outside, however, there still are some problems. One of them is the lower sensitivity for near-infrared lights due to their wider optical gap ($E_{\text{opt}}$) than c-Si. Another is a degradation of efficiency due to an increase in the number of metastable defects of the photovoltaic layer during strong-light irradiation, or the so-called Staebler-Wronski effects (SWE). Multi-junction solar cells — also sometimes called "multi-band-gap cells" — are expected to alleviate these problems. These cells consist of two or three p-i-n junctions stacked in series in the order of the i-layer $E_{\text{opt}}$ as illustrated in Fig. 1.1. Figure 1.2 shows a schematic comparison of the wavelength sensitivity of a triple-junction solar cell and a solar spectrum. Multi-junction structures allow the utilization of higher energy photons as a current at a higher voltage in the top cell with a wider $E_{\text{opt}}$ i-layer, while also absorbing lower energy photons in the bottom cell with a narrower $E_{\text{opt}}$ i-layer, as shown in Fig. 1.2. Therefore, long-wavelength sensitivity can be improved by narrowing the $E_{\text{opt}}$ of the bottom cells. Furthermore, a strong internal electric field, which is due to the thinner photovoltaic layers, prevents carrier recombination and maintains a higher fill factor after illumination than single-junction cells.

Hydrogenated amorphous silicon germanium (a-SiGe:H) alloys are considered to be good candidates as the bottom optical-absorber for double- or triple-junction solar cells, since their $E_{\text{opt}}$ can easily be narrowed by adding Ge to match the solar spectra outside. The main problem of a-SiGe:H is its deteriorating electronic properties with alloying. It is thus important to reveal the criteria in improving the material quality of a-SiGe:H, which is, however, more complicated than that of a-Si:H due to the complicated microstructure of a-SiGe:H as a ternary alloy.

1.4 Purpose of the present study

Most difficulties when dealing with a-SiGe:H alloys are caused by the intricate intertwining of
Fig. 1.1 Cross section structures of single- and multi-junction solar cells.
Fig. 1.2 Comparison of the solar spectrum and the wavelength sensitivity of a multi (triple)-junction solar cell.
the composition, $E_{\text{opt}}$ and material properties, which are particularly important in the alloys for determining solar cell performance. The purpose of the present study is to unravel the difficulty. The detailed features, as photovoltaic materials, of a-SiGe:H alloys deposited by plasma-CVD were systematically investigated with regards to both the compositions and $E_{\text{opt}}$.

Figure 1.3 illustrates a block diagram of the organization of this thesis. In Chapter 2, the film properties of a-SiGe:H including $E_{\text{opt}}$, conductivity, defect density, hydrogen bonding configurations and photostability are studied as functions of the compositions, and criteria for optimizing compositions are discussed. In Chapter 3, the hydrogen bonding configurations in a-SiGe:H, which is a factor determining both the initial properties and stability, are studied for various compositions, and the kinetic formation of microstructures and preferential hydrogen attachment are discussed. In Chapter 4, the effects of the compositions and $E_{\text{opt}}$ on the photo-induced instability of a-SiGe solar cells are investigated, and the origins of experimental observations are discussed. In Chapter 5, the progress in the performance of a-SiGe solar cells fabricated by the author's research group, to which the knowledge gained in the present study about material design was applied, is reviewed. Finally, the conclusions of the present study are summarized in Chapter 6.
Chapter 1: Introduction

Chapter 2

Deposition conditions

Electronic properties

Compositions

Optical gap

Solar cell stability against light-soaking

Chapter 3

Hydrogen bonding configurations

Chapter 4

Chapter 5

Application to efficient and stable solar cells

Chapter 6: Conclusions

Fig. 1.3 A block diagram of the organization of this thesis.
References

21. Thin film poly-crystalline silicon (poly-Si) and microcrystalline silicon (μ c-Si) deposited by plasma-CVD are other alternatives for the narrow-gap photovoltaic layer. At the present stage, however, they are not feasible yet for industrialization because the i-layer of c-Si which is an indirect transition semiconductor should be several μ m thick (1-2 order thicker than a-SiGe:H i-layer) and the deposition process for poly- and μ c-Si costs too long time.
Chapter 2
Composition Dependence of Optical Gap and Other Properties of a-SiGe:H alloys

2.1 Background

Plasma chemical vapor deposition (plasma-CVD) has been the most common technique for preparing a-Si related materials, and a-SiGe:H has been deposited from a plasma mixture of SiH₄, GeH₄ and H₂ (Fig. 2.1). The main problem of this alloy has been its poor photoelectric performance, which deteriorates rapidly with increase in the germanium atomic ratio. The deterioration, which was explained by the hydrogen preferential attachment to Si atoms¹ or by Ge–Ge clustering bonds,² was found to strongly depend on the fabrication conditions. Matsuda et al. succeeded in obtaining higher quality in a wide optical gap range, from hydrogen-diluted gas mixtures of SiH₄ and GeH₄.³ A reduction in impurities by an ultra high-vacuum (UHV) system was also reported to be effective.⁴ The deposition mechanism and the relations between the film properties and the structure of a-SiGe:H alloys are, however, less understood than those of a-Si:H, because the additional parameter, germanium, complicates the situation.

Numerous studies which relate film properties to germanium content (C₆) have been performed. For example, the optical gap (E_{opt}) of a-SiGe:H was previously reported to have a negative linear dependence on C₆ by Chevalier et al.⁵ and many other authors.⁶⁻¹¹ Smith et al., however, pointed out that this relationship did not agree with the experimental results in films deposited at different substrate temperatures.¹² This was probably due to the difference in the hydrogen content (C₇).

In the case of a-Si:H, C₇ is known to be important for determining the photoelectric properties. Papaconstantopoulos and Economou indicated a widening of the gap energy with bonded hydrogen in a quantitative simulation.¹³ A positive linear relationship between E_{opt} and C₇ has been experimentally observed by several groups including ourselves.¹⁴⁻¹⁷ Furthermore, the current study carried out by the author's group verified that most properties, namely the photo and dark-conductivities, Si–H₂/Si–H, and defect density of "device quality" film deposited from pure SiH₄
Fig. 2.1 A schematic illustration of plasma-CVD system for a-SiGe:H deposition.
plasma, were almost entirely characterized by $C_H$.\textsuperscript{17,18}

These results in a-Si:H suggest that a-SiGe:H should be regarded as a ternary alloy of silicon, germanium and hydrogen. Nevertheless, there have been few reports in which a-SiGe:H film properties were treated as functions of both $C_{Ge}$ and $C_H$. In this chapter, the photoelectric properties of a-SiGe:H films, deposited by the plasma-CVD method using SiH$_4$, GeH$_4$, and H$_2$ gas mixtures, are indicated by considering $C_H$ addition to $C_{Ge}$. A clear relationship is observed between $E_{opt}$ and the compositions. Furthermore, the guiding principle for the optimization of the alloy composition is demonstrated.

### 2.2 Experimental

The a-SiGe:H samples used in this study were prepared with a capacitively coupled RF plasma chemical vapor deposition (plasma-CVD) reactor from a gas mixture of SiH$_4$, GeH$_4$, and H$_2$. An ultrahigh vacuum (UHV) system called the "superchamber" was used to reduce the amount of impurities.\textsuperscript{19} The concentrations of oxygen, nitrogen and carbon were estimated to be $\sim 10^{18}$, $\sim 10^{17}$ and $\sim 10^{17}\text{cm}^{-3}$, respectively. The typical fabrication conditions are shown in Table 2.1. The samples for measuring optical and electronic properties were deposited on Corning #7059 glass and silver-coated glass substrates.

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The optical gap ($E_{\text{opt}}$) was determined from $h\nu$ versus $(\alpha h\nu)^{1/3}$ plots,\textsuperscript{20-22} where $\alpha$ and $h\nu$ denote the optical absorption coefficient and photon energy, respectively. The optical absorption coefficient ($\alpha$) spectra were calculated from transmittance ($T$) and reflectance ($R$) spectra, and the optical interference effect was suppressed by the $T/(1-R)$ calculation in the analysis.\textsuperscript{21} The midgap defect density ($N_p$) and characteristic energy of the Urbach tail ($E_{\text{ch}}$) were evaluated from the subgap absorption coefficient spectra measured by the constant photocurrent method (CPM).\textsuperscript{23,24} The CPM is an effective method to determine a very small optical absorption due to optical transitions between gap- and band-states by detecting the photocurrent under long-wavelength light soaking.\textsuperscript{23} The optical interference effect in the CPM spectra was also canceled by a calculation similar to that mentioned above.\textsuperscript{24} $N_D$ is assumed to be proportional to the integral of the excess absorption fitted by a Gaussian curve. The dark conductivities and photoconductivities under AM-1, 100 mW/cm$^2$ irradiation were also measured. The samples, on which aluminum coplanar electrodes were deposited, were used for the CPM and conductivity measurements. The germanium content, $C_{\text{Ge}}$ (= [Ge]/([Si]+[Ge]) atomic ratio), was determined by an X-ray photoelectron spectroscopy (XPS) method. The XPS detects the integrated intensities of energy distribution of the X-ray excited electrons from the core states (Si 2$p$ and Ge 3$d$), and $C_{\text{Ge}}$ was calibrated by using the previously reported photoionic cross sections of Si and Ge as the atomic sensitivity factors.\textsuperscript{25} The hydrogen content, $C_H$ (= [H]/([Si]+[Ge]) atomic ratio), was evaluated by combining the XPS and secondary ion mass spectroscopy (SIMS) methods, based on

$$C_H = \frac{[H]}{([\text{Si}]+[\text{Ge}])} = \alpha_{CH} \times \frac{[\text{Si}]/([\text{Si}]+[\text{Ge}])}{I(H^+)/I(28\text{Si}^+)}$$

(2.1)

where [Si]/([Si]+[Ge]) is the silicon content determined by the XPS method, and $I(H^+)$ and $I(28\text{Si}^+)$ are the peak intensities of secondary ions for masses 1 and 28, respectively. The proportionality constant, $\alpha_{CH}$, in Eq. (2.1) was estimated by comparison with an infrared (IR) absorption method. The hydrogen bonding configurations were observed using the reflectance IR absorption spectra measured for the samples on the silver-coated glass substrates and subtracted from the silver reflectance spectra. The IR absorption spectra were decomposed to the three Gaussian curves centered at the frequencies of ~1860, ~2000, and ~2100 cm$^{-1}$, which were assigned to the stretched
vibrational modes of Ge–H, Si–H, and Si–H\textsubscript{2}, respectively. The bonded hydrogen content in each configuration ($C_{H(\text{Ge-H})}$, $C_{H(\text{Si-H})}$, and $C_{H(\text{Si-H}_2)}$) was evaluated by distributing $C_H$ proportional to the product of the calibration factor ($A_{\text{Si}}$ or $A_{\text{Ge}}$) and the area under the Gaussian curve of each mode. $A_{\text{Ge}} (= 6\times10^{19}$ cm\textsuperscript{-2}) and $A_{\text{Si}} (= 1.4\times10^{20}$ cm\textsuperscript{-2}) are the previously reported A factors for the Ge–H and Si–H bonds.\textsuperscript{26} The IR absorption peaks of the Si–H mode (~2000 cm\textsuperscript{-1}) and Ge–H\textsubscript{2} mode (~1980 cm\textsuperscript{-1}) are close to each other, thus, $C_{H(\text{Si-H})}$ in this study may include the content of Ge–H\textsubscript{2}. However, some research groups fitted the IR spectrum of a-SiGe:H films precisely to four Gaussian curves assigned to the Ge–H, Ge–H\textsubscript{2}, Si–H, and Si–H\textsubscript{2} modes and suggested that the amount of Ge–H\textsubscript{2} was very small.\textsuperscript{27,28} In addition, we observed that the IR absorption peak of Ge–H\textsubscript{2} was much smaller than that of Ge–H (factor < 0.2) in a-Ge:H deposited under conditions similar to those shown in Table 2.1. For these reasons, we assumed that the amount of Ge–H\textsubscript{2} is negligible in the a-SiGe:H samples.

2.3 Deposition parameters, compositions and film properties under a constant mixture gas flow

2.3.1 $\text{GeH}_4$ flow dependence

Figures 2.2(a)-2.2(c) show the $C_{\text{Ge}}$, $C_H$, and $E_{\text{opt}}$ of the a-SiGe:H films as functions of $[\text{GeH}_4]/[\text{SiH}_4]$ flow ratio. The hydrogen dilution ratio of source gas mixture, $[\text{H}_2]/([\text{SiH}_4]+[\text{GeH}_4])$, was kept ~2.5 and $T_s$ was kept at 230°C. As $[\text{GeH}_4]/[\text{SiH}_4]$ increases, $C_{\text{Ge}}$ monotonously increases and $C_H$ slightly decreases (Figs. 2.2(a) and 2.2(b)). $E_{\text{opt}}$ decreases with increases in $[\text{GeH}_4]/[\text{SiH}_4]$ mainly due to the increase in $C_{\text{Ge}}$. $C_{\text{Ge}}$ does not have a linear relation to $[\text{GeH}_4]/[\text{SiH}_4]$ flow ratio (Fig. 2.2(a)). This is due to the difference in the incorporation ratio of Si and Ge from the source gas into the film.\textsuperscript{11} The solid line in Fig. 2.2(a) is a fitting curve by the following function,

$$C_{\text{Ge}} = p(\text{Ge}) [\text{GeH}_4]/(p(\text{Si}) [\text{SiH}_4]+p(\text{Ge}) [\text{GeH}_4])$$
Fig. 2.2 (a) Germanium content ($C_{Ge}$), (b) hydrogen content ($C_H$) and (c) optical gap ($E_{opt}$) of a-SiGe:H films as a function of the $[\text{GeH}_4]/[\text{SiH}_4]$ flow ratio. The substrate temperature ($T_s$) is constant at 230°C.
In Eq. (2.2), \( p(Si) \) and \( p(Ge) \) are the incorporation probabilities of silicon and germanium, and are defined as

\[
p(Si) = \frac{C_{Si}}{C_{gasSi}} \quad \text{and} \quad p(Ge) = \frac{C_{Ge}}{C_{gasGe}},
\]

where \( C_{gasSi} \) and \( C_{gasGe} \) are the atomic fractions of Si and Ge in the gas phase, respectively. \( p(Ge)/p(Si) = 5.9 \) was obtained by the fitting. This means that Ge atoms are 5.9 times more preferentially incorporated into the growing film from gas mixture plasma than Si atoms.

Figure 2.3 shows the photoconductivity, \( \sigma_{ph} \), and dark conductivity, \( \sigma_{d} \), of a-SiGe:H samples deposited at \( T_s = 230^\circ C \) plotted against \( E_{opt} \). \( \sigma_{ph} \) drastically decreases in the region \( E_{opt} < 1.3 \text{ eV} \) (\( C_{Ge} > \sim 40 \text{ at.\%} \)), probably due to the increase in \( N_D \) by alloying. These tendencies are qualitatively consistent to previous reports.\(^{5-7,11,28}\)

### 2.3.2 \( T_s \) and \( R_D \) dependence

Although it is known that the \( E_{opt} \) of a-SiGe:H is strongly dependent on the \([Ge]/[Si]\) atomic ratio, \( C_H \) is also important in defining the \( E_{opt} \) of a-SiGe:H. The deposition parameters, such as the substrate temperature (\( T_s \)) and the deposition rate (\( R_D \)) were found to be essential in determining \( C_H \) and film properties of a-Si:H when the effects of gas-phase polymerization or ion bombardment are not significant.\(^{18}\) Therefore, in this section, \( T_s \) and \( R_D \) during a-SiGe:H deposition were related to the film properties under a constant mixture gas flow condition. The source gas mixture ratio was fixed as \( \text{SiH}_4: \text{GeH}_4: \text{H}_2 = 30:3.2:75 \text{ (sccm)} \). This ratio was chosen because it resulted in 30-40 (at.\%) of \( C_{Ge} \), which was useful for stacked solar cells. A relatively low hydrogen-dilution ratio was used. \( R_D \) was mainly controlled by the rf power.

Figures 2.4(a)-2.4(c) show the \( C_{Ge}, C_H, \) and \( E_{opt} \) of the a-SiGe:H films as functions of \( T_s \). \( C_{Ge} \) shows little change with \( T_s \) (Fig. 2.4(a)). This indicates that the relative incorporation probability for Si and Ge atoms does not depend on \( T_s \) very much, as has already been reported.\(^{11,28}\) On the other hand, \( C_H \) decreases with the increase in \( T_s \) (Fig. 2.4(b)). This means that the growing surface reaction which determines \( C_H \) is thermally activated.\(^{29}\) The incline of \( C_H \) versus \( T_s \) is about \( 6-7 \times 10^{-2} \text{ (at.\%/K)} \). \( E_{opt} \) also goes down as \( T_s \) becomes larger (Fig. 2.4(c)). The change in \( E_{opt} \), thus, is mainly due to the change in \( C_H \).

Figures 2.5(a)-2.5(d) show that the \( C_{Ge}, C_H, E_{opt}, \) and \( \sigma_{ph}/\sigma_d \) of the a-SiGe:H films deposited
Fig. 2.3 Photoconductivity ($\sigma_{ph}$) and dark conductivity ($\sigma_{d}$) of a-SiGe:H deposited at 230°C as a function of the optical gap ($E_{opt}$).
Fig. 2.4  (a) Germanium content ($C_{\text{Ge}}$), (b) hydrogen content ($C_{\text{H}}$) and (c) optical gap ($E_{\text{opt}}$) of a-SiGe:H films as function of the substrate temperature ($T_s$). The flow ratio is constant; SiH$_4$:GeH$_4$:H$_2$ = 30:3.2:75 (sccm).
SiH$_4$: GeH$_4$: H$_2$ = 30:3.2:75 (sccm)

Fig. 2.5 (a) Germanium content ($C_{Ge}$), (b) hydrogen content ($C_H$), (c) optical gap ($E_{opt}$) and (d) photo-sensitivity ($\sigma_{ph}/\sigma_d$) of a-SiGe:H films as a function of the deposition rate ($R_D$). The flow ratio is constant; SiH$_4$:GeH$_4$:H$_2$ = 30:3.2:75 (sccm).
at various $T_s$ are plotted versus $R_D$. At each $T_s$, $C_{Ge}$ becomes smaller with increase in $R_D$ (Fig. 2.5(a)), and both $C_H$ and $E_{opt}$ increase (Figs. 2.5(b) and 2.5(c)). Thus, the dependency of $E_{opt}$ on $R_D$ is attributed to the change in both $C_{Ge}$ and $C_H$. As reasons for the $C_{Ge}$ alternation, the following two possibilities exist: (1) the radical flux density ratio $[Ge\text{ radicals}]:[Si\text{ radicals}]:[H\text{ radicals}]$ changes with rf power, because the decomposition efficiency of $GeH_4$, $SiH_4$, and $H_2$ is different from each other, (2) the incorporation probability ratio $p(\text{Ge})/p(\text{Si})$ depends on $R_D$. At present, it is not clear which of these two phenomena is a dominant factor. Stutzmann et al. reported the opposite trend ($C_{Ge}$ rises with rf power) in non-diluted $SiH_4$ and $GeH_4$ deposition system. This different tendency may be due to variations in the gas ($SiH_4$ and $GeH_4$) dissolving rate or radical sticking coefficient with $H_2$ dilution, or it may be due to the limited radical feeding by the source gas flow rate in one of the cases. When $R_D$ goes up, the time permitted for surface reactions, such as the hydrogen-eliminating reaction on the growing surface, becomes shorter, and this causes higher $C_H$ in the film (Fig. 2.5(b)). At low $R_D$ (< 40 Å/min) and low $T_s$ (= 230°C), $C_H$ seems to be saturated (Fig. 2.5(b)).

At high $R_D$ (> 100 Å/min), $\sigma_{ph}/\sigma_d$ was improved at all $T_s$ (230, 270, and 320°C), due to the large decrease in $C_{Ge}$ (Fig. 2.5(a)). Noticing the low $R_D$ (< 80 Å/min) range, in which the varieties of $C_{Ge}$ should be small (see Fig. 2.5(a)), a decrease in $R_D$ causes the $\sigma_{ph}/\sigma_d$ of a-SiGe:H films to advance at $T_s$ = 230°C, to change slightly at $T_s$ = 270°C, and to decline at $T_s$ = 320°C. The lower $R_D$ is generally considered to correspond to higher film qualities, since the time available for network relaxation in the growing surface becomes longer. However, the results in Fig. 2.5(d) indicate that it depends on $T_s$. It is supposed that an excess of the hydrogen-eliminating reaction on the growing surface led to the film quality degrading at high $T_s$ (= 320°C).

In the case of a-Si:H deposition from pure $SiH_4$ plasma, Hishikawa et al. reported that an optimum $R_D$ which corresponds to the minimum defect density exists for every $T_s$, and that the optimum $R_D$ becomes higher for higher $T_s$. This is because the film properties are determined by the balance between the surface reaction velocity (which has a positive relation with $T_s$) and the time available for the surface reaction (which has a negative relation with $R_D$). This effect seems to be similar to that in Fig. 2.5(d).
2.4 Optical gap as a function of $C_H$ and $C_{Ge}$

Figure 2.6 shows $E_{\text{opt}}$ versus $C_{Ge}$ for samples in which $T_s$ and the rf power were constant ($T_s = 230^\circ \text{C}$ and rf power density $= 20 \text{ mW/cm}^2$), and only the gas mixture ratio $[\text{GeH}_4]/[\text{SiH}_4]$ varied ($\text{SiH}_4:\text{GeH}_4:\text{H}_2 = 30:0-3.2:75 \text{ (sccm)}$). The $E_{\text{opt}}$ of a-SiGe:H in Fig. 2.6 follows the relation,

$$E_{\text{opt}} = a C_{Ge} + b \text{ (eV)}, \quad (2.3)$$

which has been reported by several authors,\textsuperscript{5-11} and is partly enumerated in Table 2.2 where $E_{\text{Tauc}}$ in the table is the optical gap determined by the Tauc's plot.\textsuperscript{31} The coefficient $a$ for $C_{Ge}$ in Eq. (2.3), which is estimated to be about $-0.78 \text{ (eV)}$ from Fig. 2.6, is consistent with the other authors' results (see Table 2.2). But, it has been pointed out that this linear relation could not represent the $E_{\text{opt}}$ of films deposited at different $T_s$ from each other,\textsuperscript{12} and we also mentioned this above (see Figs. 2.4(c) and 2.5(c)). This disagreement is most likely due to the difference in $C_H$.

Figure 2.7 indicates the $E_{\text{opt}}$ contour map of a-SiGe:H films deposited at various $T_s$ (120-320$^\circ \text{C}$), rf power (10-100 mW/cm$^2$), and gas mixture ratios ($\text{SiH}_4:\text{GeH}_4:\text{H}_2 = 30:2-5.2:75 \text{ (sccm)}$), as a function of $C_H$ and $C_{Ge}$. Each symbol represents a composition with a close $E_{\text{opt}}$ value. It can be seen that $E_{\text{opt}}$ is determined by the combination of $C_H$ and $C_{Ge}$. The variations in the $E_{\text{opt}}$ of a-Si:H, a-Ge:H, and a-SiGe:H ($C_{Ge}=0.35-0.40$) with the $C_H$ are plotted in Fig. 2.8. $C_H$ of the a-Si:H and a-Ge:H samples was determined from IR absorption spectra. The $E_{\text{opt}}$ seems to have an almost linear relationship with both $C_H$ and $C_{Ge}$, as shown by the solid lines in Fig. 2.7 and the meshed lines in Fig. 2.8, and can be represented by the following equation.

| Table 2.2 Previously reported dependence of $E_{\text{Tauc}}$ on $C_{Ge}$* |
|-----------------|-----------------|
| Mackenzie et al.$^7$ | $E_{\text{Tauc}} = -0.78C_{Ge} + 1.76 \text{ (eV)}$ |
| Chen et al.$^8$ | $E_{\text{Tauc}} = -0.74C_{Ge} + 1.74 \text{ (eV)}$ |
| Wagner et al.$^9$ | $E_{\text{Tauc}} = -0.7C_{Ge} + 1.7 \text{ (eV)}$ |
Fig. 2.6  Optical gap ($E_{\text{opt}}$) of a-SiGe:H deposited at 230°C as a function of the germanium content ($C_{\text{Ge}}$).
Fig. 2.7 Optical gap ($E_{opt}$) contour map of a-SiGe:H deposited at various temperatures and gas flow ratios as a function of the germanium content ($C_{Ge}$) and hydrogen content ($C_{H}$).
Fig. 2.8 Optical gap ($E_{\text{opt}}$) of a-Si:H (open circle), a-Ge:H (open triangle) and a-SiGe:H (open square) as a function of the hydrogen content ($C_H$).
\[ E_{\text{opt}} = 1.3C_H - 0.6C_{\text{Ge}} + 1.4 \ (\text{eV}). \] (2.4)

The absolute coefficient of \( C_{\text{Ge}}, -0.6, \) in Eq. (2.4) is smaller than \(-0.78\) from Fig. 2.6. A part of the change in \( E_{\text{opt}} \) with \( C_{\text{Ge}} \) in Fig. 2.6 should be ascribed to the variation in \( C_H \), which is known to decrease with the increase in \( C_{\text{Ge}} \) at a fixed \( T_s \) and rf power \(^{32,33}\) as shown in Figs. 2.2(a) and 2.2(b). \( C_{\text{Ge}} \) does not make much difference on the gradient of \( E_{\text{opt}} \) versus \( C_H \) in Fig. 2.8. Disregarding the existence of atomic vacancies or voids, and the transition of the film rigidness caused by the difference in \( C_H \), the widening of \( E_{\text{opt}} \) with \( C_H \) is due to the valence band energy being pushed down because the Si–H (3.35eV) or Ge–H (2.99eV) bonds are stronger than Si–Si (1.83eV) or Ge–Ge (1.63eV) bonds. \(^{13,34-36}\) An increase in the bond energy per hydrogen atom, caused by switching Si–Si bonds to Si–H bonds, or Ge–Ge bonds to Ge–H bonds, can be respectively represented as follows,

\[ E(\text{Si–H}) - E(\text{Si–Si})/2 \doteq 2.4 \ (\text{eV}), \] (2.5)

\[ E(\text{Ge–H}) - E(\text{Ge–Ge})/2 \doteq 2.2 \ (\text{eV}), \] (2.6)

where \( E(X–Y) \) indicates \( X–Y \) bond energy. The nearness of these two values is probably the reason why the incline of \( E_{\text{opt}} \) to \( C_H \) is only slightly dependent on the [Ge]/[Si] atomic ratio. Although the physical grounds are insufficient, Eq. (2.4) shows good agreement with the experimental results in a wide range of \( C_{\text{Ge}} \) as a first order approximation (see Fig. 2.8). Generally, the tendency has been to indicate a-SiGe:H film properties as functions of \( C_{\text{Ge}} \) or \( E_{\text{opt}} \). However, a clearer demonstration can be expected by using the functions of \( C_H \) and \( C_{\text{Ge}} \) as shown in Fig. 2.7, with regarding a-SiGe:H as a ternary alloy of silicon, germanium and hydrogen.

2.5 Optimized composition for a certain optical gap (\( E_{\text{opt}} = 1.32 \) eV)

In designing solar cells, \( E_{\text{opt}} \) of the photovoltaic layer is an essential factor which should be
optimized beforehand, because it limits the output current and voltage of the devices. However, $E_{\text{opt}}$ of a-SiGe:H depends strongly on not only $C_{\text{Ge}}$ but also $C_{\text{H}}$ and follows a linear function of $C_{\text{H}}$ and $C_{\text{Ge}}$, as pointed out in the previous section. For this reason, a-SiGe:H samples with various combinations of $C_{\text{H}}$ and $C_{\text{Ge}}$ can have the same $E_{\text{opt}}$. However, their electronic properties can differ from each other due to variations in their composition. In this section the optimum composition was investigated for a-SiGe:H with a certain $E_{\text{opt}}$ for stable solar cells. The properties of both films and p-i-n devices were compared among samples with constant $E_{\text{opt}}$ and various compositions. The film properties and performance of solar cells before and after light soaking were investigated. The results were related to the $C_{\text{H}}$ and hydrogen bonding configurations.

2.5.1 Composition dependence of film properties

a-SiGe:H films with the same $E_{\text{opt}}$ and various compositions were prepared. The substrate temperature and $[\text{SiH}_4]/[\text{GeH}_4]$ flow ratio were carefully controlled by the combinations of $C_{\text{Ge}}$ and $C_{\text{H}}$ to keep $E_{\text{opt}}$ constant. A relatively low hydrogen dilution was used: the dilution ratio, $[\text{H}_2]/([\text{SiH}_4]+[\text{GeH}_4])$ was kept at $\approx$2.5. The samples were 300-500 nm thick. $E_{\text{opt}}$ of 1.32eV (which corresponds to 1.4-1.45eV by Tauc's method) was chosen in this study because it is empirically known to be suitable as the bottom i layer of double- or triple-junction stacked solar cells. Figure 2.9 shows the relationship between $C_{\text{H}}$ and $C_{\text{Ge}}$ for the samples in which $E_{\text{opt}}$ is constant at 1.32±0.005 eV. $E_{\text{opt}}$ of these samples approximately follows Eq. (2.4). The sample with more $C_{\text{H}}$ contains more $C_{\text{Ge}}$ because of the constant $E_{\text{opt}}$. Figures 2.10(a)-2.10(c) show $\sigma_{\text{ph}}$, $\sigma_{\text{d}}$, $E_{\text{ch}}$, and $N_{\text{D}}$ as functions of $C_{\text{H}}$. More than 10 at.% of $C_{\text{H}}$ results in deterioration of $\sigma_{\text{ph}}$ and $\sigma_{\text{d}}$ (Fig. 2.10(a)). The $C_{\text{H}}$ values for both the minimum $E_{\text{ch}}$ and the minimum $N_{\text{D}}$ exist at $\approx$10 at.%, and they are close to each other (Figs. 2.10(b) and 2.10(c)). A similar correspondence between the $N_{\text{D}}$ and $E_{\text{ch}}$ for a-Si:H has also been reported.\(^{37,38}\) To explain this tendency, Stutzmann has ascribed the initial $N_{\text{D}}$ in a-Si:H to the equilibrium of the weak-bond state and the dangling-bond state which arises from the breaking of weak Si-Si bonds.\(^{37}\) The correlation between $E_{\text{ch}}$ and $N_{\text{D}}$ in Figs. 2.10(b) and 2.10(c) is quantitatively consistent with Stutzmann's bond-breaking model.

Figure 2.11 illustrates the bonded hydrogen content in the different configurations, such as
Fig. 2.9 The relationship of the germanium content ($C_{Ge}$) and hydrogen content ($C_{H}$) for a-SiGe:H with a constant optical gap ($E_{opt}$) of 1.32 eV.
Fig. 2.10  (a) The photoconductivity ($\sigma_{ph}$) and dark conductivity ($\sigma_{d}$), (b) the characteristic energy of the Urbach tail ($E_{ch}$), and (c) the defect density ($N_D$) of the a-SiGe:H samples with a constant $E_{opt}$ (~1.32 eV) as functions of the hydrogen content ($C_H$).
Fig. 2.11  The bonded hydrogen content of a-SiGe:H samples with a constant $E_{\text{opt}}$ ($\sim$1.32eV) in different configurations, such as Si-H, Si-H$_2$, and Ge-H, as functions of the total hydrogen content ($C_H$).
$C_{H(Ge-H)}$, $C_{H(Si-H)}$, and $C_{H(Si-H_2)}$ determined from IR absorption spectra, as a function of the total hydrogen content, $C_H$. The amount of hydrogen bonded to germanium, $C_{H(Ge-H)}$, is much less (factor 5) than that to silicon, $(C_{H(Si-H)} + C_{H(Si-H_2)})$, although $C_{Ge}$ of these samples is 30-45 at.% (Fig. 2.9). This is due to the preferential attachment of hydrogen to silicon rather than to germanium as previously reported.\textsuperscript{1,27} The dependence of $C_{H(Ge-H)}$ on $C_H$ is weaker than that of $(C_{H(Si-H)} + C_{H(Si-H_2)})$ on $C_H$, and thus, it is suggested that the difference in film properties shown in Figs. 2.10(a)-2.10(c) is caused by the hydrogen bonded to silicon. The most important role of the hydrogen in a-Si alloys is (a) to terminate dangling bonds and (b) to relax the bonding network. In the region where $C_H$ is lower than 8 at.%, the lack of hydrogen debases these functions, and $E_{ch}$ and $N_D$ increase (Figs. 2.10(b)-2.10(c)). On the other hand, the dihydride hydrogen content, $C_{H(Si-H_2)}$, monotonically increases with the increase in $C_H$, while the monohydride hydrogen contents, $C_{H(Ge-H)}$ and $C_{H(Si-H)}$ are almost constant (Fig. 2.11). Too much Si-H\textsubscript{2} degrades the electronic and structural properties in the region where $C_H$ is higher than 12 at.% (Figs. 2.10(b) and 2.10(c)). The balance between the defect termination and structural relaxation due to added hydrogen atoms, and the deterioration caused by the increasing density of Si-H\textsubscript{2} determine the optimum $C_H$ at around 10 at.\% in the system of $E_{opt}$=1.32eV. Generally, for a-Si:H deposited by the ordinary plasma-CVD method, $C_H$ of $\sim$15 at.% is considered to be appropriate. The optimum $C_H$ of $\sim$10 at.% for the a-SiGe:H samples is smaller than the value for a-Si:H. This may be due to the preferential attachment of hydrogen to silicon over germanium. a-SiGe:H contains more $C_{H(Si-H_2)}$ than a-Si:H, when their $C_H$ is the same, because the larger number of hydrogen atoms provided per silicon atom in a-SiGe:H raises the probability of existence of Si-H\textsubscript{2}. Therefore, in a-SiGe:H, the deterioration in the high $C_H$ region occurs more swiftly and the suitable $C_H$ is lower than in a-Si:H. More details of the inhomogeneous hydrogen bonding configurations in a-SiGe:H are discussed in Chapter 3.

2.5.2 Composition dependence of cell performance

These a-SiGe:H films with constant $E_{opt}$ were applied to the i layers of a-SiGe single-junction and a-Si/a-SiGe double-junction solar cells, which consisted of TCO/ p(a-SiC:H)/ i(a-SiGe:H)/ n(a-Si:H)/ metal, and TCO/ p(a-SiC:H)/ i(a-Si:H)/ n(a-Si:H)/ p(a-SiC:H)/ i(a-SiGe:H)/ n(a-Si:H)/ metal,
respectively. The thin and flat-gap a-SiGe:H was used for the i layer. Figure 2.12 indicates the initial conversion efficiency of a-SiGe single-junction solar cells under red light (1sun AM-1.5 with an optical filter "R65", which sharply cuts out the light wavelengths shorter than 650nm) as a function of $C_H$ of the i layer. The i-layer thickness of these cells was constant at ~150 nm. The variation in the conversion efficiency is mainly due to that of the fill factor ($FF$). An optimum $C_H$ ~10 at.% also exists for the maximum conversion efficiency. The tendencies of the conversion efficiency in Fig. 2.12 reflect those of $N_D$ (see Fig. 2.10(c)), which control the recombination loss of generated carriers in the i-layer and affect the conversion efficiency via $FF$.

In addition to $N_D$, $E_{opt}$, which limits the built-in potential and the number of absorbed photons, also affects the conversion efficiency via the product of the open circuit voltage ($V_{oc}$) and the short-circuit current ($I_{sc}$), — and probably via $FF$ as well. Using an experimental system in which only the substrate temperature or [SiH$_4$]/[GeH$_4$] flow ratio is changed, a composition for the lowest $N_D$ will also be observed, but this will not always offer the highest conversion efficiency because of the variation of $E_{opt}$. The influence of $N_D$ upon the conversion efficiency becomes even smaller when the i layer becomes thinner, because the stronger internal electric field tends to keep $FF$ higher. In this study, in spite of the thin i-layer, a very clear correspondence was observed between the film properties and the cell performance, because the constant $E_{opt}$ kept $V_{oc}$, $I_{sc}$, and the internal electric field constant.

The optimum composition of a-SiGe:H for the initial properties of both films and solar cells was observed for the constant $E_{opt}$ (Figs. 2.10 and 2.12). For photovoltaic materials, however, the stability against light irradiation is also an important factor. Figure 2.13 shows the normalized conversion efficiency, which is the value divided by the initial conversion efficiency, of a-SiGe single-junction solar cells after red light soaking for 0.25, 6 and 140 hours (5 sun, AM-1.5 with R65 filter at 48°C under open circuit condition) as a function of $C_H$ of the i layer. The normalized conversion efficiency against almost has a negative linear relation to $C_H$, and the incline against $C_H$ becomes larger with greater light soaking time. This means that the degradation ratio of the solar cell becomes lager with the increase in $C_H$ (or $C_{Ge}$) of the i-layer. These results suggest that the incorporated hydrogen or Si-H$_2$ (which increases with $C_H$, as shown in Fig. 2.11) enhances or
Fig. 2.12 The initial conversion efficiency of a-SiGe single-junction solar cells with a constant $E_{\text{opt}}$ (~1.32 eV) under red light illumination (1 sun, AM-1.5 through R65 optical filter) as a function of the hydrogen content of the i layer.
Fig. 2.13 Normalized conversion efficiency, which is the value divided by the initial conversion efficiency, of a-SiGe single-junction solar cells after red light soaking for 0.25, 6 and 140 hours (5 sun, AM-1.5 with R65 filter at 48°C under open circuit condition) as a function of $C_H$ of the i layer.
assists the creation of light-induced defects, although the effect of Ge is not revealed yet. More
details of the effects of compositions on the stability are discussed in Chapter 4. Consequently, the
optimum compositions are believed to shift to the lower $C_H$ region, though the amount of the shift
depends on the degradation conditions such as the light intensity, light soaking time, temperature
and i-layer thickness. The world’s most efficient solar cells applied this concept to cell design are
introduced in Chapter 5.

2.6 Summary

A detailed study of a-SiGe:H films deposited by a plasma-CVD method using SiH$_4$, GeH$_4$, and
H$_2$ gas mixtures has been demonstrated with paying careful attention to its composition: both $C_H$
and $C_{Ge}$. Furthermore, the properties have been compared among a-SiGe:H films and solar cells
with a constant optical gap of 1.32 eV and different combinations of $C_H$ and $C_{Ge}$.

(1) Concerning the correlation of film properties with deposition conditions, (a) $C_{Ge}$ depends only
slightly on $T_s$ and decreases with a rise in rf power, (b) $C_H$ increases with a decrease in $T_s$ or an
upturn of $R_D$, (c) the optimum $R_D$, which corresponds to the maximum photo-sensitivity, depends
on $T_s$.

(2) $E_{opt}$ is controllable by changing $T_s$ and $R_D$, in addition to the $[\text{GeH}_4]/[\text{SiH}_4]$ source gas mixture
ratio, and can be expressed by a linear function of $C_H$ and $C_{Ge}$. As a result, films with different
compositions can have the same $E_{opt}$.

(3) The optimum composition for initial properties, such as the Urbach tail characteristic energy,
defect density, and conversion efficiency of solar cells, was determined for a certain $E_{opt}$ ($= 1.32$
eV). These tendencies can be explained in terms of the hydrogen bonding configuration.

(4) The optimum composition for a certain $E_{opt}$ shifts to the lower $C_H$ region after light soaking
due to the larger degradation for higher $C_H$ samples. This suggests that hydrogen or Si-H$_2$ plays an
important role in light-induced degradation.
References

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Chapter 3
Inhomogeneous Hydrogen Bonding Structures in a-SiGe:H

3.1 Background

Incorporated H atoms and their bonding structures are important for determining the properties of a-Si alloys. It has been often reported that material qualities such as photo-conductivity, defect density and photo-stability of a-Si related materials deteriorate with increasing dihydride concentration ([Si–H$_2$]), evaluated by the decomposition of IR absorption peaks centered at ~2000 and ~2100 cm$^{-1}$.\textsuperscript{1-6} The H content, $C_H$, in the material is one of the key factors determining the H bonding structure in a-Si:H deposited by plasma CVD, partly because the probability of multiple H atoms bonding to one Si atom increases with $C_H$. Indeed, many previous studies have already reported that [Si–H$_2$]/[Si–H] has a 1 on 1 positive correlation to $C_H$ for a-Si:H deposited by various deposition systems such as plasma CVD or magnetron sputtering method.\textsuperscript{2-7} Another important factor is the process condition. For example, it is known that [Si–H$_2$] can be reduced independently from $C_H$ by the use of highly H$_2$-diluted SiH$_4$ plasma or post H-plasma treatment.\textsuperscript{3,6} In this way, quantitative comprehension of the H bonding configurations in a-Si:H has been steadily progressing.

a-SiGe:H is a tetrahedrally bonding semiconductor as well as a-Si:H. It has also been suggested that Si–H$_2$ configurations in a-SiGe:H films cause the deterioration of the photoelectric properties of the materials and solar cell performances including stability against light exposure.\textsuperscript{4,11} However, the H bonding structure in a-SiGe:H is much less understood than that of a-Si:H due to the feature of H atoms selectively bonding to Si rather than to Ge, so-called "preferential attachment."\textsuperscript{12-14} This feature is believed to cause a microscopic inhomogeneity in the network and to deteriorate the electronic properties of the alloys. The preferential attachment is probably due to the smaller binding energy of H–Ge than that of H–Si. However, the detailed mechanisms determining the preference of H bonding and the deterioration of material properties are not clear yet.

The purpose of the study in this chapter is to reveal the principle of H bonding in device-quality
a-SiGe:H alloys deposited by rf plasma CVD from SiH$_4$, GeH$_4$ and H$_2$ mixture gas. The correlations between the H bonding configurations and $C_H$ of a-SiGe:H alloys with various compositions were systematically investigated. In order to separately consider the microstructures around Si and Ge, the author focuses on the $C_H$ per host atom, namely Si or Ge. The results of a-SiGe:H are discussed by comparing with those of a-Si:H and hydrogenated amorphous germanium (a-Ge:H). The origin of H bonding preference is also mentioned in connection with the deposition kinetics. Furthermore, the construction mechanism of H–Si bonding structures is also discussed.

### 3.2 Experimental

a-SiGe:H films with various compositions were prepared in a UHV (ultra high vacuum) rf plasma reactor from a gas mixture of SiH$_4$, GeH$_4$ and H$_2$. The deposition conditions are shown in Table 3.1. The a-SiGe:H films of 2000-5000 Å thick were deposited simultaneously on Corning #7059 glass substrates for optical and compositional measurements, and on silver-coated glass substrates for infrared reflectance absorption spectroscopy (IR-RAS) measurement. $C_{Ge}$ ($=[Ge]/([Si]+[Ge])$ atomic ratio) was determined by the X-ray photoelectron spectroscopy (XPS) method. $C_H$ was evaluated by combining the XPS and secondary ion mass spectroscopy (SIMS) methods. The H bonding configurations were observed using the reflectance IR absorption spectra measured for the samples on the silver-coated glass substrates and subtracted from the silver reflectance spectra. The details of these composition analysis were shown in Chapter 2 (see 2.2.

<table>
<thead>
<tr>
<th>Table 3.1 Deposition conditions of samples.</th>
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<tr>
<td>Substrate temperature</td>
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<td>Reaction pressure</td>
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<tr>
<td>Background pressure</td>
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<td>RF power density</td>
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<td>Hydrogen dilution ratio</td>
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3.3 Composition dependence of hydrogen bonding configurations

3.3.1 \textit{H–Si bonding configurations in a-Si:H and a-Ge:H}

Figure 3.1 shows the microstructure factor of a-Si:H, \([\text{Si–H}_2]/[\text{Si–H}]\), deposited from low-diluted ([H\(_2\)]/[SiH\(_4\)] < 2.5) and high-diluted ([H\(_2\)]/[SiH\(_4\)] > 10) source gases plotted against \(C_H\). [Si–H\(_2\)]/[Si–H] for the low-diluted a-Si:H samples has 1 on 1 correlations to \(C_H\), as previously reported.\(^5\)\(^-\)\(^{13}\) The [Si–H\(_2\)]/[Si–H] ratio can be reduced independently from \(C_H\) by the use of high dilution. Figure 3.2 shows the microstructure factor of a-Ge:H, [Ge–H\(_2\)]/[Ge–H], deposited from diluted source gases ([H\(_2\)]/[GeH\(_4\)] = 10) plotted against \(C_H\). [Ge–H\(_2\)]/[Ge–H] in a-Ge:H also has 1 on 1 correlations to \(C_H\) and increases more drastically with \(C_H\) than that of a-Si:H, in spite of the higher dilution ratio. This is partly because the a-Ge:H samples with high \(C_H\) (> 7 at.\%) should have been deposited at very low temperatures (< 100\(^\circ\)C). When deposited at higher temperatures than 150 \(^\circ\)C, the \(C_H\) and [Ge–H\(_2\)]/[Ge–H] of a-Ge:H are less than 8 at.% and 0.2, respectively.

3.3.2 \textit{H–Si bonding configurations in a-SiGe:H}

The bonding H contents per host atom for Si and Ge in a-SiGe:H were defined respectively as follows,

\[
C_{H(Si)} = ([\text{Si–H}_2]+[\text{Si–H}])/[\text{Si}],
\]

\[
C_{H(\text{Ge})} = [\text{Ge–H}]/[\text{Ge}].
\]

Here, the relation, \(C_H = (1-C_{\text{Ge}})\times C_{H(Si)} + C_{\text{Ge}} \times C_{H(\text{Ge})}\), follows. Figure 3.3 shows the relationship between \(C_{H(Si)}\) and \(C_{H(\text{Ge})}\) in a-SiGe:H with various compositions. \(C_H\) in the films were widely varied by changing the substrate temperature from 80 to 350\(^\circ\)C. One can see that only \(C_{H(Si)}\) increases with increasing \(C_H\), and \(C_{H(\text{Ge})}\) is almost constant at 2-4 at.%. The results in Fig. 3.3 suggest that the differences of H–Si bonding structure are more dominant than H–Ge when
Fig. 3.1  $[\text{Si-H}_2]/[\text{Si-H}]$ plotted against $C_H$ for a-Si:H deposited from low-diluted ($[\text{H}_2]/[\text{SiH}_4] < 2.5$) and highly diluted ($[\text{H}_2]/[\text{SiH}_4] > 10$) source gases. The arrow indicates a schematic trend when increasing dilution ratio.
Fig. 3.2  \([\text{Ge-H}_2]/[\text{Ge-H}]\) plotted against \(C_H\) for a-Ge:H deposited from diluted source gases ([H\(_2\)/[GeH\(_4\)] = 10). \(C_H\) was controlled by varying the process temperature from room temperature to 300°C.
Fig. 3.3  The relationship between $C_{H(Si)} (=([Si-H_2]+[Si-H])/[Si])$ and $C_{H(Ge)} (= [Ge-H]/[Ge])$ in a-SiGe:H with $C_{Ge} = 30-60$ at.%. 

\textbf{a-SiGe:H} \\
$C_{Ge}$ (at.%) \\
Ts=80-350°C \\
\begin{itemize}
  \item 30-35  \\
  \item 35-40  \\
  \item 40-46  \\
\end{itemize}

$C_H$ increase

Normalized H content bonding to Si, $C_{H(Si)}$ (at.%) \\
Normalized H content bonding to Ge, $C_{H(Ge)}$ (at.%)
comparing the a-SiGe:H samples with various $C_H$. The author thus focused on the H–Si bonding configurations in a-SiGe:H. Figure 3.4 shows the $[\text{Si–H}_2]/[\text{Si–H}]$ of a-SiGe:H samples deposited from low-diluted ($[\text{H}_2]/([\text{SiH}_4]+[\text{GeH}_4] = 2.5$) and high-diluted ($[\text{H}_2]/([\text{SiH}_4]+[\text{GeH}_4] = 20-40$) mixture gases as a function of $C_{\text{H(Si)}}$. The broken line in Fig. 3.4 indicates the $[\text{Si–H}_2]/[\text{Si–H}]-C_H$ trend of low-diluted a-Si:H replotted from Fig. 3.1. The $[\text{Si–H}_2]/[\text{Si–H}]-C_{\text{H(Si)}}$ correlation of the low-diluted a-SiGe:H is similar to the $[\text{Si–H}_2]/[\text{Si–H}]-C_H$ correlation of a-Si:H. In addition, $[\text{Si–H}_2]/[\text{Si–H}]$ of a-SiGe:H can be reduced by the high H$_2$-dilution of the source gas as well as a-Si:H.

For H–Si bonds in a-SiGe:H alloys, the $[\text{Si–H}_2]/[\text{Si–H}]-C_{\text{H(Si)}}$ correlation of both low- and high-diluted samples is similar to the $[\text{Si–H}_2]/[\text{Si–H}]-C_H$ correlation in a-Si:H, as shown in Fig. 3.4. This suggests that the construction mechanism of the H–Si bonding structure of a-SiGe:H during deposition, including the effect of high H$_2$ dilution, is approximately the same as that of a-Si:H. There also exists, however, a minor quantitative difference. The H–Si configurations in a-SiGe:H are more insensitive to the H$_2$-dilution than that of a-Si:H. In order to obtain the dilution effect on the $[\text{Si–H}_2]/[\text{Si–H}]$ shown in Fig. 3.4, larger dilution ratios (>20) and higher rf power density (>300 mW/cm$^2$) were needed, although the dilution ratios of ~5, and the rf power density of ~30 mW/cm$^2$ are effective enough for a-Si:H. This is consistent with previous studies which have reported that the optimum dilution-ratio$^{14,15}$ and process temperature$^{2,16}$ for a-SiGe:H are higher than those for a-Si:H. The IR absorption peak at ~2100 cm$^{-1}$ is generally attributed to the stretching vibration mode of dihydride (Si–H$_2$) bonds including (Si–H$_2$)$_n$ chains, although there is still another opinion that ascribes the origin of the peak to the surface-like configuration which consists of H atoms terminating the inner wall of voids.$^2$ However, the similarity of the $[\text{Si–H}_2]/[\text{Si–H}]-C_{\text{H(Si)}}$ correlation of a-SiGe:H to the $[\text{Si–H}_2]/[\text{Si–H}]-C_H$ correlation of a-Si:H suggests that the peak is mainly caused by the Si–H$_2$ configuration rather than by the voids.

### 3.3.3 Origin of material deterioration with alloying

Figure 3.5 shows $C_H$, $C_{\text{H(Si)}}$ and $C_{\text{H(Ge)}}$ for a-SiGe:H plotted against $C_{\text{Ge}}$. $C_{\text{Ge}}$ was controlled by varying GeH$_4$ flow ratio with keeping the process temperature constant at 230°C. Figure 3.6 shows the change in the $[\text{Si–H}_2]/[\text{Si–H}]-C_{\text{H(Si)}}$ correlation as $C_{\text{Ge}}$ increases.

The deterioration of electronic properties when adding Ge has been often attributed to the
Fig. 3.4  \([\text{Si-H}_2]/[\text{Si-H}]\) plotted against \(C_{H(Si)}\) for a-SiGe:H samples deposited from low-diluted \((\text{[H}_2]/(\text{[SiH}_4]+\text{[GeH}_4]) = 2.5)\) and highly-diluted \((\text{[H}_2]/(\text{[SiH}_4]+\text{[GeH}_4]) = 20-40)\) mixture gases. The broken line indicates the \([\text{Si-H}_2]/[\text{Si-H}]-C_H\) trend of low-diluted a-Si:H replotted from Fig. 3.1.
Fig. 3.5 $C_H$, $C_{H(Si)}$ and $C_{H(Ge)}$ of a-SiGe:H plotted against $C_{Ge}$. $C_{Ge}$ was controlled from 0 to 60 at.% by varying GeH$_4$ flow ratio with keeping the process temperature constant at 230$^\circ$C.
Fig. 3.6  [Si-H₂]/[Si-H] plotted against $C_{H(Si)}$ for a-SiGe:H with various $C_{Ge}$ (0-60 at.%) deposited from low-diluted source gases ($[H_2]/([SiH_4]+[GeH_4] = 2.5$). The arrow indicates a schematic trend when increasing $C_{Ge}$. 
preferential H attachment to Si,$^{12-14}$ which causes a lack of H–Ge bonds and the insufficient termination of Ge dangling bonds. However, when increasing $C_{\text{Ge}}$, $C_{\text{H(Si)}}$ and $[\text{Si–H}_2]/[\text{Si–H}]$ increase in contrast to the slight decrease of $C_{\text{H}}$ as shown in Figs. 3.5 and 3.6. Thus, the increase in Si–H$_2$ bonds is thought to also partly cause the deterioration of film properties. Concerning the photo-stability, Stutzmann et al. reported that the metastable dangling bond (DB) defects created by exposing prolonged illumination are mainly Si oriented DB, although most of the initial defects are Ge oriented DB.$^{17,19}$ This selective creation of the metastable Si DB is also explainable by the increasing Si–H$_2$ bonds. This is because the Si–H$_2$ introduced by alloying reduces the average network coordination of Si and seems to enhance the structural flexibility selectively around Si atoms.

$C_{\text{H(Si)}}$ and $[\text{Si–H}_2]/[\text{Si–H}]$ in a-SiGe:H are thought to be determined by the H-elimination reactions during film growth as well as a-Si:H, which have been reported to be not simple H–Si breaking but a combined reaction to Si–Si or H$_2$ formation because its activation energy is much smaller than the H–Si binding energy.$^{17}$ The increasing $C_{\text{H(Si)}}$ and $[\text{Si–H}_2]/[\text{Si–H}]$ with $C_{\text{Ge}}$ as shown in Figs. 3.5 and 3.6 suggest that the existence of Ge atoms, bonding to less H, prevents the H-elimination reactions between H–Si bonds. The suppressed H-elimination reactions consequently retain more H–Si bonds in the bulk and cause Si–H$_2$ structures with increasing $C_{\text{Ge}}$. This is also probably the reason why additional energy for surface reactions is demanded for high-quality a-SiGe:H via higher process temperatures, or higher ratios of H$_2$ dilution than for a-Si:H, as mentioned previously.$^{1,4}$

### 3.3.4 Origin of preferential attachment

The preferential H attachment coefficient, $P$, is defined by the following equation,$^{12,13}$

$$P = \frac{C_{\text{H(Si)}}/C_{\text{H(Ge)}} = ([\text{Si–H}_2]+[\text{Si–H}]) \times [\text{Ge}])/([\text{Ge–H}] \times [\text{Si}])}{([\text{Si–H}_2]+[\text{Si–H}]) \times [\text{Ge}])/([\text{Ge–H}] \times [\text{Si}]以外}{(3.3)}$$

Figure 3.7 shows the $P$ of a-SiGe:H deposited at various substrate temperatures (replotted data from Fig. 3.3) plotted against $C_{\text{H}}$. $P$ increases from 3 to 11 with an increase in $C_{\text{H}}$ from 5 to 17 at.%. Figure 3.8 shows the $P$ of a-SiGe:H deposited at 230°C (replotted data from Fig. 3.5) plotted against $C_{\text{Ge}}$. $P$ increases again from 3 to 8 with an increase in $C_{\text{Ge}}$ from 2 to 56 at.%.
Fig. 3.7  \( P \) of a-SiGe:H deposited at various substrate temperatures (replotted data from Fig. 3.3) plotted against \( C_H \). \( C_H \) was controlled by changing the substrate temperature from 80 to 350°C.
Fig. 3.8  $P$ of a-SiGe:H deposited at 230°C (replotted data from Fig. 3.5) plotted against $C_{Ge}$. $C_{Ge}$ was controlled by changing $[GeH_4]/[SiH_4]$ flow ratio.
$P$ of a-SiGe:H prepared by rf plasma CVD or rf sputtering has been previously reported to be $\sim 10$ by Paul et al.,$^{12}$ $\sim 5$ by Stutzmann et al.$^{19}$ $\sim 3-6$ by Wakagi et al.$^{20}$ $\sim 2-4$ by Rudder et al.$^{21}$ and to be $\sim 3$ by Schroeder et al.$^{22}$ $P$ is a well normalized value to remove the effect of the difference in Ge/Si ratio, and indicates that how many times H atoms are statistically more easily bonded to Si over Ge in the alloy. Therefore, they argued that a certain $P$ value exists independently of the compositions.$^{22}$ In other words, there seemed to be a constant difference between the statistical bonding probability of H atoms to Si and to Ge. However, according to the results shown in Figs. 3.7 and 3.8, $P$ values have positive correlations to both $C_H$ and $C_{Ge}$. In addition, $C_{H(Ge)}$ is almost constant at $2-4$ at.% independently of both $C_H$ and $C_{Ge}$, as shown in Figs. 3.3 and 3.5. Thus, it might be an error to assume the existence of the critical $P$ value determined simply by the difference of H bonding probabilities. These results suggest that the critical value determining the preferential attachment is not $P$ but $C_{H(Ge)}$.

The author interprets the origin of the preference of H bonding from the viewpoint of the film growth kinetics as follows. Figure 3.9 shows schematic illustrations of the growing surface of a-SiGe:H (left) and the depth profiles of $C_{H(Ge)}$ and $C_{H(Si)}$ (right). (1) The main precursors contributing to a-SiGe:H film deposition are polyhydride radicals such as $SiH_3^*$ and $GeH_3^*$. Thus, the topmost surface of the growing film is covered by H atoms supplied by those radicals.$^{17}$ (2) During several atomic-layer growth, surplus H atoms are eliminated from H–Si bonds in the layers under the topmost surface, so-called "growth zone", and $C_{H(Si)}$ decreases with film growth to reach a value of the bulk a-SiGe:H as well as suggested for a-Si:H.$^{23}$ As a result, $C_{H(Si)}$ strongly reflects growing conditions such as the process temperature. (3) H is eliminated much faster from H–Ge bonds at the growing surface because of the smaller binding energy (which means a shorter time constant for chemical reaction) than that of H–Si bonds.$^{24}$ Thus, $C_{H(Ge)}$ rapidly reaches to the steady-state value for the bulk, independently of the growing conditions. (4) Consequently only $C_{H(Si)}$ changes with $C_H$, and $P$ is strongly dependent on $C_H$ and $C_{Ge}$. The points of this model are that the H-elimination reaction around Ge atoms occurs quickly to minimize $C_{H(Ge)}$, and the reactions in the growth zone such as H elimination and H rebinding mainly occur only around Si atoms. In other words, the thickness of the growth zone for Ge is much smaller than that for Si (Fig. 3.9).

This model is consistent to recent experimental observations by in-situ reflective IR absorption
Fig. 3.9  Schematic illustration of the a-SiGe:H film growth deposited by rf plasma CVD. SiH$_3$* and GeH$_3$* radicals flying from source gas plasma regions stick to the surface of the growing film and become bulk via H elimination and network construction in the growth zone. H atoms bonding to Ge are released faster than those to Si, which means that the growth zone of Ge is thinner than that of Si. Therefore, $C_{H(\text{Ge})}$ rapidly reaches to solubility-limited value below 5 at.%. (See text.)
spectroscopy on growing a-SiGe:H film. Toyoshima et al. reported that the behavior of thermal H desorption from surface Si–hydride species of Si rich alloys is similar to that of a-Si:H. Nakagawa et al. also suggested that $C_{H(\text{Ge})}$ is determined in a much shorter time (or much thinner zone from the topmost surface) than that of Si–H. Turning now to the origin of the constant $C_{H(\text{Ge})}$, Jackson et al. and Acco et al. suggested that there exists a solubility-limited $C_{H}$ in a-Si:H, which is associated with the concentration of defect-related deep H trap. They reported the solubility-limited $C_{H}$ values of ~5 at.% and 3-4 at.% respectively, by H evolution experiments. These values for a-Si:H are consistent to 2-4 at.% of $C_{H(\text{Ge})}$ for the bulk a-SiGe:H. The solubility-limited $C_{H}$ values (< 5 at.%) is a minimum $C_{H}$ in order to maintain a rigid amorphous network (with less dihydride bonds or void structures) in a mixture of the fourfold Si or Ge and univalent H atoms. This is supposed to be the reason why $C_{H(\text{Ge})}$ in a-SiGe:H is determined independently from deposition conditions.

3.4 Are H–Si bonding structures random?

The similarity of the $[\text{Si–H}_{2}]/[\text{Si–H}].C_{H(\text{Si})}$ correlation of a-SiGe:H (Fig. 3.4) to the $[\text{Si–H}_{2}]/[\text{Si–H}].C_{H}$ correlation of a-Si:H (Fig. 3.1) was pointed out in 3.3.2. This suggests that there exists a common rule determining H–Si bonding structures in both a-Si:H and a-SiGe:H.

"Randomness" was traditionally considered to be a useful model to describe a-Si structure. Because the non-equilibrium structure of amorphous materials seems to be determined by the atomic arrangement corresponding to the maximum entropy. Schubert et al. compared the relative concentrations of Si–Si, Si–Ge and Ge–Ge bonds, and suggested that the tetrahedral matrix arrangement of Si–Ge is approximately random in a-SiGe:H. Lucovski et al. and Gaspari et al. have respectively tried to describe H bonding structures as a function of $C_{H}$ by statistical considerations assuming the random arrangement of H and Si atoms in the solid. Although these random models have succeeded to qualitatively explain the increase in $[\text{Si–H}_{2}]$ with $C_{H}$, there still remains a quantitative missing link. For example, it is well known that $[\text{Si–H}_{2}]$ can be reduced independently from $C_{H}$ by the use of deposition techniques such as highly H$_{2}$-diluted SiH$_{4}$ plasma or post H-plasma treatment. The previous random models could not explain these transitions in
H structures depending on the deposition conditions. Randomness probably stands up for materials fabricated by rapid cooling from its liquid-phase. However, at most \(-300^\circ C\) of the a-Si:H deposition temperature is much less than its melting point of 1412°C. Under these non-equilibrium conditions, the structure of a-Si:H is affected not only by the randomness but also by the growth kinetic. The purpose of this section is to discuss the construction mechanism of H–Si bonding structures.

3.4.1 Two numerical random models

Figure 3.10 schematically illustrates the growth process of a-Si:H film. SiH$_3^*$ and H$^*$ radicals generated in the plasma come flying and stick to the growing surface. Then, the topmost of the growing film is covered by H atoms, and $C_H$ of this region is 200-300 at.%. After several atomic-layer growth, $C_H$ reached a steady state value of bulk at 10-20 at.%. and H configurations were fixed. Important reactions in the growth zone are (a) the distortion of excess H atoms and (b) the reconstruction of H bonding structures including H insertion from the hydrogen-rich surface. In order to analytically describe the construction kinetics of H–Si bonding structures, the author proposes two random models simulating these two reactions. One is based on the assumptions of (A) random H-elimination from SiH$_3$ radicals, and the other on (B) random H-insertion and mixing reaction into Si network, respectively. These random models are compared to the experimental results given in 3.3.2.

**Model A: Random H-elimination**

It was assumed that each Si atom on the growing topmost is bonding to three H atoms and H bonding configurations are determined simply by H-elimination reaction from H–Si bonds with atomic unit. There are three possible H-elimination reactions as follows,

$$\text{Si–H}_x \rightarrow \text{Si–H}_{x-1} + H \quad (x=1, 2, 3). \quad (3.4)$$

If H atoms randomly eliminate from each configuration, the possibility of that a certain H-detachment reaction occurs following each x value in Eq. (3.4) can be represented as $C_{\text{Si–H}_x}/C_H$ ($x=1, 2, 3$). Where $C_{\text{Si–H}_x}$ is H content of Si–H$_x$ configuration and $\sum C_{\text{Si–H}_x} = C_H$. In these
Fig. 3.10  Schematic illustration of H reactions in the growing a-Si:H surface. The hydrogen content ($C_H$) and bonding configurations in a-Si:H are considered to be determined by the hydrogen elimination and insertion reactions.
reactions, when Si–H\textsubscript{x} vanishes Si–H\textsubscript{x-1} is simultaneously created. The decreasing ratios of \( C_{\text{Si–H}_x} \) (x=1, 2, 3) with decreasing \( C_H \) can be represented as follows, respectively,

\[
\frac{dC_{\text{Si–H}_3}}{dC_H} = 3\frac{C_{\text{Si–H}_3}}{C_H},
\]

(3.5)

\[
\frac{dC_{\text{Si–H}_2}}{dC_H} = 2\frac{C_{\text{Si–H}_2}}{C_H} - 2\frac{C_{\text{Si–H}_3}}{C_H},
\]

(3.6)

\[
\frac{dC_{\text{Si–H}}}{dC_H} = \frac{C_{\text{Si–H}_1}}{C_H} - \frac{C_{\text{Si–H}_2}}{C_H}.
\]

(3.7)

These simultaneous differential equations, Eq. (3.5)-(3.7), can be solved under the following boundary conditions,

\[
C_{\text{Si–H}_x} | \quad C_H = 0 \quad (x = 1, 2), \quad C_{\text{Si–H}_3} | \quad C_H = 3 = 3,
\]

(3.8)

\[
C_{\text{Si–H}_x} | \quad C_H = 0 \quad (x = 1, 2, 3).
\]

(3.9)

\( C_H = 3 \) in Eq. (3.8) indicates the topmost condition of the growing film where SiH\textsubscript{3} radicals pour on. The solutions can be represented as follows,

\[
C_{\text{Si–H}_3} = \frac{C_H^3}{9},
\]

(3.10)

\[
C_{\text{Si–H}_2} = -2C_H^2(C_H - 3)/9,
\]

(3.11)

\[
C_{\text{Si–H}_1} = C_H(C_H - 3)^2/9.
\]

(3.12)

Thus, the [polyhydride]/[monohydride] ratio of this random H-elimination model can be represented as a function of \( C_H \) as follows,

\[
(C_{\text{Si–H}_3} + C_{\text{Si–H}_2})/C_{\text{Si–H}} = -C_H(C_H - 6)/(C_H - 3)^2.
\]

(3.13)
**Model B: random H-insertion**

H-Si bonding structure in a-Si:H network is assumed to be determined by randomly driving H atoms into Si network and/or by randomly mixing of Si and H atoms. In this random network composed of \( M \) fourfold Si atoms and \( L \) univalent H atoms, assuming that all H atoms combine with Si atoms and the number of dangling bonds is negligible compared to \( M \) and \( L \), the number of Si–H bonds, \( N_{Si-H} \), and Si–Si bonds, \( N_{Si-Si} \), can be represented as

\[
N_{Si-H} = L = M C_H, \tag{3.14}
\]

\[
N_{Si-Si} = (4M-L)/2 = M(4-C_H)/2, \tag{3.15}
\]

where \( C_H = L/M \). The probability of a bond sampled from the network at random being a Si–Si bond, \( p_{Si-Si} \), and a H–Si bond, \( p_{H-Si} \), is represented as follows, respectively,

\[
p_{Si-Si} = N_{Si-Si} / (N_{Si-H} + N_{Si-Si}) = (4-C_H)/(4+C_H), \tag{3.16}
\]

\[
p_{H-Si} = 1-p_{Si-Si} = 1-N_{Si-Si} / (N_{Si-H} + N_{Si-Si}) = 2C_H/(4+C_H). \tag{3.17}
\]

When a H atom is sampled from the network at random, the probability of the configuration of the H–Si bond being the mono-hydride—in other words, the rest three folds of the Si atom connected with the neighboring Si—is \( p_{Si-Si}^3 \). In the similar consideration, H content in different configurations can be represented as,

\[
C_{Si-H} = C_H p_{Si-Si}^3 = C_H(4-C_H)^3/(4+C_H)^3, \tag{3.18}
\]

\[
C_{Si-H_2} = 3C_H p_{H-Si} p_{Si-Si}^2 = 6C_H^2(4-C_H)^2/(4+C_H)^3, \tag{3.19}
\]

\[
C_{Si-H_3} = 3C_H p_{H-Si}^2 p_{Si-Si} = 12C_H^3(4-C_H)/(4+C_H)^3, \tag{3.20}
\]

\[
C_{Si-H_4} = C_H p_{H-Si}^3 = 8C_H^4/(4+C_H)^3. \tag{3.21}
\]
Thus, \([\text{polyhydride}] / [\text{monohydride}]\) ratio of this random H-insertion model can be represented as a function of \(C_H\) as follows,

\[
(C_{\text{Si-H}_2} + C_{\text{Si-H}_3} + C_{\text{Si-H}_4}) / C_{\text{Si-H}} = \frac{(1-p_{\text{Si-Si}}^3)p_{\text{Si-Si}}^3}{(4-C_H)^3} = 2C_H(C_H^2 + 48)/(4-C_H)^3. \tag{3.22}
\]

This result is quantitatively consistent with that obtained by Gaspari et al. through a statistical computer simulation.\(^{10}\)

### 3.4.2 Comparison to the experimental results

Figures 3.11(a) and 11(b) show Si-H\(_x\) contents (\(x=1, 2\) and 3) of the random H-elimination model (Model A) described by Eqs. (3.10)-(3.12) as functions of \(C_H\). Figures 3.12(a) and 12(b) show Si-H\(_x\) contents (\(x=1, 2, 3\) and 4) of the random H-insertion model (Model B) described by Eqs. (3.18)-(3.21) as functions of \(C_H\). Although these two models brought qualitatively similar results, the random H-elimination causes less polyhydride structures than the random H-insertion model in the region with \(C_H\) less than 30 at.\%. Figure 3.13 shows [polyhydride]/[monohydride] ratios of Model A and Model B described respectively by Eqs. (3.13) and (3.22) as functions of \(C_H\). The hatched regions indicate the experimental results of high and low diluted a-Si:H samples, respectively, shown in Fig. 3.1. One can see that the low diluted samples selectively contain polyhydride bonds and that the high diluted samples approximately correspond to the random models (Fig. 3.14). Under the low diluted conditions, H-insertion is not significant and H-elimination is dominant. Although atomic-unit random reactions were assumed in Model A, the low diluted conditions are thought to allow only limited reactions with relatively small activation energy. The actual H abstraction reactions are not simple H–Si bond breaking but the combined reactions with Si–Si or H–H bond formation.\(^{18}\)

Thus, the reaction rate of H distortion reaction is considered to depend on the network around the H-Si bond. The reactions from monohydride and dihydride configurations can be represented as follows,

\[
\text{Si}_3\text{SiH} + \text{H} \rightarrow \text{Si}_3\text{Si} + \text{H}_2 \uparrow, \tag{3.23}
\]
Fig. 3.11 Si-H\textsubscript{x} contents (x=1, 2 and 3) of the random H-elimination model (Model A) described by Eqs. (3.10)-(3.12) as functions of \( C_H \): (a) \( C_H = 0-30 \) at.\%, (b) \( C_H = 0-300 \) at.\%.
Fig. 3.12  Si-H$_x$ contents (x=1, 2 and 3) of the random H-insertion model (Model B) described by Eqs. (3.18)-(3.21) as functions of $C_H$: (a) $C_H = 0$-30 at.%, (b) $C_H = 0$-300 at.%. 

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Fig. 3.13 [polyhydride]/[monohydride] ratios of Model A and Model B described respectively by Eqs. (3.13) and (3.22) as functions of $C_H$. The hatched regions indicate the experimental results of high and low diluted a-Si:H samples, respectively, shown in Fig. 3.1.
**Process Condition Dependence of H bonding Structures in a-Si:H**

<table>
<thead>
<tr>
<th>Deposition conditions</th>
<th>Energy for surface reaction</th>
<th>H bonding structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low dilution</td>
<td>Small</td>
<td>Selective SiH₂ formation</td>
</tr>
<tr>
<td>High dilution</td>
<td>Large</td>
<td>Random</td>
</tr>
</tbody>
</table>

**The reason of selective SiH₂ formation**

- **SiH₂ → SiH + H**
  - Activation energy: large
  - Reaction rate: slow
- **SiH → Si + H**
  - Activation energy: small
  - Reaction rate: fast

Fig. 3.14 A summary of process condition dependence of hydrogen bonding configurations in a-Si:H.
Sato et al. and Srinivasan et al. respectively reported that the activation energy of H abstraction from monohydride (Eq. (3.23)) is smaller than that from dihydride (Eq. (3.24)) by \textit{ab initio} simulations\textsuperscript{30,31} and the reaction rate of (Eq. (3.23)) is much faster than that of (Eq. (3.24))\textsuperscript{31}. These are probably the reason of preferential polyhydride formation under low diluted process (Fig. 3.14).

On the other hand, the high diluted deposition processes are thought to apply enough energy to cause H-elimination and insertion reactions by the H radicals or ions pouring on. An active reconstruction of the amorphous network caused by these reactions results in the random H bonding configurations which give the largest entropy of the arrangement of H atoms.

### 3.5 Summary

The composition dependencies of H bonding configurations in a-SiGe:H alloy films with various compositions deposited by rf plasma CVD were systematically investigated by comparisons to a-Si:H and a-Ge:H. Conclusions drawn in this chapter are summarized below.

1. As $C_H$ increases from 7 to 27 at.\% by varying the substrate temperature from 80 to 350\degree C, the normalized H content per Si atom ($C_{H(Si)}$) in a-SiGe:H drastically increases with $C_H$, while the normalized H content per Ge atom ($C_{H(Ge)}$) is almost constant at 2-4 at.\%. This suggests that the structural differences of a-SiGe:H with $C_H$ are mainly caused in the regions around Si atoms.

2. When focusing on H–Si bonds, $[\text{Si–H}_2]/[\text{Si–H}]-C_{H(Si)}$ correlations in a-SiGe:H deposited from both low- and high- diluted source gases are equivalent with those in a-Si:H. This suggests that the construction mechanism of H bonding structures around Si atoms in a-SiGe:H is similar to that in a-Si:H.

3. As $C_{Ge}$ increases from 0 to 60 at.\% at a constant substrate temperature of 230\degree C, only $C_{H(Si)}$ increases form 10 to 14 at.\%. The increase in $C_{H(Si)}$ with $C_{Ge}$ is considered to be caused by the existence of Ge atoms which prevent H-elimination reactions around Si atoms. This increase in $C_{H(Si)}$ indirectly causes an increase in $[\text{Si–H}_2]/[\text{Si–H}]$ and a material deterioration by alloying.
(4) The preferential attachment coefficient, \( P = \frac{C_{H(\text{Ge})}}{C_{H(\text{Si})}} \), has positive correlations to both \( C_H \) and \( C_{\text{Ge}} \). The \( P \) value is considered to be determined not simply by the statistical difference of the bonding probabilities of H to Si and to Ge, but by the kinetics of H elimination during film growth. The \( C_{H(\text{Ge})} \) value is supposed to be solubility limited, while the \( C_{H(\text{Si})} \) value is surface reaction limited.

(5) Two random models were proposed to describe the construction kinetics of H–Si bonding structures, and these models were compared to the experimental results. H-bonding configurations of high-diluted samples are almost random. On the other hand, H-bonding configurations of low-diluted samples are not random but selectively contains polyhydride bonds.
References

Chapter 4
Effects of i-layer Optical Gap and Compositions on a-SiGe Solar Cell Stability

4.1 Background

One of the main problems of a-Si based solar cells is a decline in efficiency due to an increase in the number of metastable defects in the photovoltaic layer during light irradiation, or the so-called Staebler-Wronski effect (SWE).\(^1\) As mentioned in Chapter 1, multi-junction solar cells should relieve this problem because each photovoltaic layer is thinner than that of single-junction solar cells, and a strong internal electric field prevents carrier recombination and maintains a higher fill factor after illumination. In addition to the cell structure, the stability of the materials themselves must also be improved. It is thus necessary to clarify the origin of the light-induced changes in a-Si alloys. For instance, optical gap ($E_{\text{opt}}$), hydrogen and impurities are considered to play a role in the defect creation mechanism.\(^2\)

The unstable kinetic behavior of a-Si alloys exposed to illumination is believed to be caused not by a direct optical excitation from bonding into antibonding states, but by the recombination of photo-generated carriers. This is because, for example, it has been confirmed that current injection also causes a degradation similar to light soaking.\(^2\) Metastable dangling bonds are thought to be created by the breaking of weak bonds in amorphous networks. Here, the non-radiative recombination of photo-excited hole-electron pairs, via trapping in the valence- and conduction-band tails, provides the energy for breaking weak bonds. Thus, $E_{\text{opt}}$ is probably a dominant factor in the light-induced defect creation process, because the recombination energy, a trigger for photo-induced structural change, should depend on $E_{\text{opt}}$. Indeed, many previous reports have suggested that a-Si:H and its alloy materials with narrower $E_{\text{opt}}$ are more stable.\(^3-11\) A research group from Princeton Univ. reported that the saturated defect density of a-Si:H and a-SiGe:H after prolonged illumination tends to decrease slightly with a decrease in $E_{\text{opt}}$.\(^3-5\) Bauer \textit{et al}. analyzed photodegradation behavior in the conductivity of a-Si:H, a-SiGe:H and a-SiC:H, and noted longer time decay for narrower $E_{\text{opt}}$.\(^7\) Unold \textit{et al}. theoretically predicted that no degradation should occur
in a-SiGe:H with $E_{\text{opt}}$ less than a certain value.\textsuperscript{10} In these previous studies, however, not enough attention was paid to the effect of compositions, such as hydrogen content ($C_{H}$) or germanium content ($C_{Ge}$), which are strongly correlated to $E_{\text{opt}}$\textsuperscript{12} a-Si:H with a narrower $E_{\text{opt}}$ contains a smaller amount of hydrogen, and the $E_{\text{opt}}$ of a-SiGe:H is generally reduced by increasing the germanium atomic ratio. Therefore, the effects of hydrogen and the energy gap on stability could not be separated clearly in experiments using a-Si:H system. In particular, $C_{H}$ and hydrogen bonding configurations are considered to be an important factor affecting the light-induced degradation process.\textsuperscript{13-18}

There is another uncertain factor concerning the origin of the effect of $E_{\text{opt}}$ on photostability. This is the contributing effect of $E_{\text{opt}}$ on annealing kinetics. The degradation behavior of a-Si alloys is determined by the balance of the defect creation and annealing processes. If the energy barrier from the metastable state to the annealed state becomes smaller with a decrease in $E_{\text{opt}}$, annealing may be activated and seemingly smaller degradation may result. The comprehension of defect annealing kinetics is thus as important as the comprehension of defect creation mentioned above. To the author's knowledge, studies have yet to be carried out on the $E_{\text{opt}}$ dependence of the annealing process of a-SiGe:H alloys.

The purpose of this chapter is to clarify the effects of the i-layer $E_{\text{opt}}$ on a-SiGe solar cell stability. a-SiGe single-junction solar cells with various $E_{\text{opt}}$ and those with a constant $E_{\text{opt}}$ and various combinations of $C_{H}$ and $C_{Ge}$ were prepared. The degradation behavior among the samples with various $E_{\text{opt}}$ and those with constant $E_{\text{opt}}$ and various compositions were systematically compared to distinguish the contribution of $E_{\text{opt}}$ from the effect of compositions. Cells with various $E_{\text{opt}}$ were recovered by annealing at various temperatures after light soaking. Their behavior during recovery was also systematically analyzed to separate the effects of $E_{\text{opt}}$ on the creation and removal of metastable defects. The main focus was put on the variation of the decay time-constants of the degradation and recovery processes. Furthermore, the effect of $E_{\text{opt}}$ on the temperature dependence of solar cell stability is also discussed together with connecting the effect to defect creation and annealing kinetics.
4.2 Experimental

a-SiGe single-junction solar cells with a constant $E_{\text{opt}}$ and various combinations of $C_H$ and $C_{Ge}$ were used, as mentioned in Chapter 2. a-SiGe single-junction solar cells with various $E_{\text{opt}}$ were also prepared. The cells consisted of a TCO/p(a-SiC:H)/i(a-SiGe:H)/n(a-Si:H)/metal structure. A-SiGe:H was deposited using a rf plasma reactor from a gas mixture of SiH$_4$, GeH$_4$ and H$_2$. The thickness of the i-layer was ~1000 Å. A-SiGe:H films of 2000-3000 Å thick were also prepared on Corning #7059 substrates to monitor the optical and compositional properties. More details of the sample preparation and evaluation are given in Chapter 2.

4.3 Degradation ratio

4.3.1 Composition dependence of light-induced degradation

Figure 4.1 schematically illustrates the $E_{\text{opt}}$ contour map of a-SiGe:H as a function of $C_H$ and $C_{Ge}$. Following Eq. (2.4), the correlation among $C_H$, $C_{Ge}$ and $E_{\text{opt}}$ is represented as a plate painted with various tones, shown in Fig. 4.1. Each tone on the plate indicates a region in which $E_{\text{opt}}$ is close. The three arrows on the plate show the directions in which the materials are supposed to become more stable.

Arrow I shows the direction along which $E_{\text{opt}}$ decreases when $C_{Ge}$ increases. In this case, $C_H$ does not strongly depend on $C_{Ge}$ if the substrate temperature is constant, as shown in Chapter 3. Arrow II shows the direction along which $E_{\text{opt}}$ decreases by reducing $C_H$ in a-Si:H. As mentioned above, materials have been reported to become more stable in the directions of both arrows I and II. However, it has not yet been confirmed that hydrogen is a dominant factor in the case of arrow I, because $E_{\text{opt}}$ also decreases. The $C_H$ dependence of the degradation behavior of a-SiGe solar cells with constant $E_{\text{opt}}$ and different compositions was shown in Fig. 2.10. Arrow III shows the direction in which $C_H$ decreases while $E_{\text{opt}}$ was kept constant, as shown in Fig. 2.10. The fact that the materials become more stable in the direction of arrow III, in which the effect of $E_{\text{opt}}$ is free, supports the assumption that decrease in $C_H$ contributes to at least partly stabilizing the materials in arrow I also. This also confirms the contributing effect of incorporated hydrogen or its bonding
Fig. 4.1 Schematic illustration of $E_{\text{opt}}$ contour map of a-SiGe:H as a function of $C_H$ and $C_{\text{Ge}}$. Three arrows show the directions in which materials are considered to become more stable. (See text.)
structure to the creation of metastable defects. In other words, metastable defect density can be reduced by decreasing $C_H$.

There is still the possibility of the participation of $CG_{c•}$ which increases with $C_H$ in the direction of arrow III, because the Ge–Ge or Ge–H bonds are weaker and break easier than Si–Si or Si–H bonds. However, this kind of effect from increasing $CG_{c•}$ would seem to be relatively small — at least smaller than the effect of the band gap — if a-SiGe:H alloys with higher $CG_{c•}$ and lower $E_{opt}$ are more stable, as was previously suggested.

A number of kinetic models\(^2\) which were proposed to explain the Staebler-Wronski effects of a-Si have linked to the motion of incorporated hydrogen, which is a small, univalent atom and is considered to move easily within the tetrahedral network. The likeliest suggestion is that the hydrogen moves to and stabilizes metastable defects, which arise from the breakage of weak Si-Si bonds during light exposure, by attaching itself to one of a pair of dangling bonds or by coordinating a three-centered Si-H-Si configuration (Fig. 4.2).\(^{13,19-21}\) Thus, too many hydrogen atoms or Si–H\(_2\) configurations are supposed to enhance the motion of hydrogen atoms during light soaking, besides they decrease the average fold number of Si networks, and consequently cause more metastable defects.

4.3.2 Optical gap dependence of light-induced degradation and thermally-induced recovery

Figure 4.3 shows the cell efficiency normalized by the initial efficiency after white light soaking. The efficiency is plotted against the $E_{opt}$ of i-layers. After 70 minutes, the cells with $E_{opt} = 1.4-1.5$ eV showed the most degradation. However, after 7500 minutes, the minimum normalized efficiency shifted to the region of $E_{opt} = 1.2-1.3$ eV. Here, we should note that, in the i-layer with narrower $E_{opt}$, (1) the carrier generation rate is larger, and (2) the concentration of carrier generation on the incident side is more radical, because of the higher photon absorption coefficient. To cancel the influence of these factors, the same set of cells was also degraded under filtered light. Filters sharply cut the short-wavelength part of the 5 sun, AM-1.5 light, and a cut wavelength was selected for each $E_{opt}$ of the i-layers in order to keep the short-circuit current at 35-40 mA/cm\(^2\). Figure 4.4 shows the cell efficiency normalized by the initial efficiency after filtered light soaking. The minimum again shifted to the narrower $E_{opt}$ region during the filtered light soaking, as in Fig. 4.3. The minimum shifts shown in Figs. 4.3 and 4.4 mean that cells with narrower $E_{opt}$ degrade
Fig. 4.2 Schematic illustrations of a hydrogen-mediated model of the reversible Staebler-Wronski effects.
Degradation conditions:
5 sun, 25°C, open circuit

Fig. 4.3 The normalized efficiency of a-SiGe single-junction cells after 70, 1000 and 7500 minutes of white light soaking (5 sun, AM-1.5 light with open circuit conditions at 25 °C) plotted against the $E_{opt}$ of i-layers.
Degradation conditions:
5 sun with optical filters to keep $J_{sc} \sim 40 \text{mA/cm}^2$, 25°C, open circuit

![Graph showing normalized efficiency of a-SiGe single-junction cells after 160, 5000, and 10000 minutes of filtered light soaking plotted against $E_{opt}$ of i-layers. The filters sharply cut the short-wavelength part of the 5 sun, AM-1.5 light, and a cut wavelength was selected for each $E_{opt}$ of i-layers to keep the short-circuit current at 35-40 mA/cm$^2$.]

Fig. 4.4 The normalized efficiency of a-SiGe single-junction cells after 160, 5000, and 10000 minutes of filtered light soaking plotted against $E_{opt}$ of i-layers. The filters sharply cut the short-wavelength part of the 5 sun, AM-1.5 light, and a cut wavelength was selected for each $E_{opt}$ of i-layers to keep the short-circuit current at 35-40 mA/cm$^2$. 
Recovery conditions:
Dark, 150°C, open circuit

Fig. 4.5 The normalized efficiency of a-SiGe single-junction cells during dark annealing at 150°C, plotted against $E_{\text{opt}}$ of i-layers.
slower.

The cells degraded under white light were recovered by thermal annealing at 150 °C. Figure 4.5 shows the cell efficiency normalized by the initial efficiency during annealing, plotted against annealing time. In contrast to the case of degradation, no peak shift was observed. After 1000 minutes of annealing, the efficiency of all samples recovered to more than 95% of their initial values.

4.4 Time constant analysis for defect creation and annealing

The degradation and recovery of the solar cell efficiency are thought to occur due to the creation and removal, respectively, of metastable defects in the i layers. To clearly understand the degradation and recovery behavior in cell performance, the time-dependent data of cell efficiency were related to the change of defect density.

4.4.1 Definition of time constant

Previous experimental results suggested that the cell efficiency or fill factor during light-induced degradation has a linear relationship to the logarithm of the defect density.\(^{22-24}\) For example, Chen and Yang reported the following empirical relation,\(^{24}\)

$$\eta \propto 1 - A \log N,$$

(4.1)

where $\eta$, $A$ and $N$ are, respectively, the efficiency, constant depending on the cell structure and defect density of i-layer.

The term "degradation ratio," meaning the ratio of decreasing conversion efficiency, is generally used to describe the stability of a-Si materials. However, the "degradation ratio" not only reflects the stability of materials, but also the stability of the device structure. For example, cells with thinner i-layers exhibit smaller degradation. The differences of cell structure appear as variations in "A" in Eq. (4.1). In order to extract the effect of the material factor by canceling $A$, the normalized efficiency ($\eta_N$) was defined as follows using Eq. (4.1),

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\[ \eta_N = \left( \eta - \eta_{\text{sat}} \right) / \left( \eta_{\text{init}} - \eta_{\text{sat}} \right) \]

\[ = \log \left( N / N_{\text{sat}} \right) \log \left( N_{\text{init}} / N_{\text{sat}} \right), \]  

where \( \eta_{\text{init}}, \eta_{\text{sat}}, N_{\text{init}} \) and \( N_{\text{sat}} \) are the initial and saturated efficiency and defect density, respectively.

Figure 4.6 shows a kinetic model of the creation and removal of metastable defects during light-soaking and thermal-annealing. The changing rate of defect density is believed to be determined by a trade-off among the following four processes: light-induced creation (LIC), light-induced annealing (LIA), thermal-induced creation (TIC), and thermal-induced annealing (TIA). Redfield proposed the following relationship to describe defect creation kinetics,\textsuperscript{25,26}

\[ \frac{dN}{dt} = C_1 (N_1 - N) R - C_2 N R + \nu_1 (N_1 - N) - \nu_2 N, \]  

(4.3)

where \( N_1 \) and \( R \) are, respectively, the total density of potential defect sites and the recombination rate of light-generated carriers, and \( C_1, C_2, \nu_1 \) and \( \nu_2 \) are constants corresponding to LIC, LIA, TIC, and TIA. The time dependence of \( N \) can be represented by the following stretched-exponential function,

\[ N = N_{\text{sat}} - (N_{\text{sat}} - N_{\text{init}}) \exp \left( - \left( t / \tau \right)^\beta \right), \]  

(4.4)

where \( \tau \) and \( \beta \) are constants. Although \( \beta=1 \) is the solution of Eq. (4.3), the values \( 0 < \beta < 1 \) have been reported previously from an experimental fitting.\textsuperscript{26} When assuming \( R=0 \), Eqs. (4.3) and (4.4) respectively become the rate equation and its solution, which were proposed by Kakalios \textit{et al.}\textsuperscript{27} expressing the reduction of defect density during annealing in the dark. Thus, Eq. (4.3) can represent the saturation behavior that not only increases defect density during light-soaking, but also decreases defect density during annealing.

Using Eqs. (4.2) and (4.4), the time dependence of \( \eta_N \) during light-soaking or dark annealing can be represented as,
\[
\frac{dN}{dt} = C_1(N_t - N)R - C_2NR + V_1(N_t - N) - V_2N
\]

Solution: \( N(t) = N_{sat} - (N_{sat} - N_{init})\exp(-t/\tau)^\beta \)

\[
\tau = \frac{1}{(C_1 + C_2)R + V_1 + V_2}
\]

\[
N_{sat} = \frac{N_t (C_1R + V_1)}{(C_1 + C_2)R + V_1 + V_2}
\]

Fig. 4.6 A kinetic model of the creation and removal of metastable defects during light-soaking and thermal-annealing. (See text.)
\[ \eta_N = (\eta - \eta_{\text{sat}})/(\eta_{\text{init}} - \eta_{\text{sat}}) = - (1/n) \log[1 - (1 - 1/10^n) \exp(- (t/\tau)\beta)], \]  

(4.5)

where \( n = \log (N_{\text{sat}}/N_{\text{init}}) \). To quantitatively discuss the photostability of i-layer materials, the main focus is put on the time constant, \( \tau \), in which the cell-structure constant "A" is canceled, as shown in Eq. (4.5).

4.4.2 Effect of optical gap and composition on the time constant for degradation

Figure 4.7 shows the efficiency normalized by the initial and saturated values of a-SiGe solar cells with constant \( E_{\text{opt}} \) and different compositions plotted against the AM 1.5, 5 sun light soaking time at 25°C. The solid lines in Fig. 4.7 are the fitting curves of Eq. (4.5). Here, we assumed \( n = 2 \), which corresponds to the increase in defect density from \( 10^{15} \) to \( 10^{17} \) cm\(^{-3} \) to be saturated during light soaking. \( \eta_{\text{sat}} \) and \( \tau_{\text{LIC}} \) (\( \tau \) for light-induced defect creation) and \( \beta \) for each \( E_{\text{opt}} \) were estimated from the fitting curves. There are about 1.5 orders of magnitude difference in \( \tau_{\text{LIC}} \) between 1.20 eV and 1.58 eV cells, even taking into account the fitting errors. The larger \( \tau_{\text{LIC}} \) for the narrower \( E_{\text{opt}} \) cell is consistent with the results in the previous report which indicates that the rate of decrease in photo-conductivity becomes lower with the narrowing of \( E_{\text{opt}} \).

A clear correlation has been observed between the degradation time constant, \( \tau_{\text{LIC}} \), and the i-layer \( E_{\text{opt}} \), as shown in Fig. 4.7. However, while \( E_{\text{opt}} \) changes, the compositions also change. To clarify the effect of the difference in \( C_H \) and \( C_{\text{Ge}} \) on \( \tau_{\text{LIC}} \), the degradation behavior of a-SiGe solar cells with a constant \( E_{\text{opt}} \) (~1.32 eV) and various combinations of \( C_H \) and \( C_{\text{Ge}} \) were also compared. Figure 4.8 shows the efficiency of these cells normalized by the initial and saturated values, plotted against light soaking time. When \( C_H, C_{H(Si-H_2)} \) and \( C_{\text{Ge}} \) were changed while \( E_{\text{opt}} \) was kept constant, no composition dependence of \( \tau_{\text{LIC}} \) for light-induced degradation was observed. This result indicates that difference in \( C_H, C_{H(Si-H_2)} \) and \( C_{\text{Ge}} \) has very little effect on the degradation time constant, \( \tau_{\text{LIC}} \).

4.4.3 Effect of optical gap on the time constant for recovery

Cells with various \( E_{\text{opt}} \) i-layers were recovered by thermal annealing at various temperatures after 1000 minutes of light-soaking. Figure 4.9 shows cell efficiency normalized by the values
Degradation conditions:
5 sun, 25°C, open circuit

Light soaking time (min)

Normalized efficiency 
((\eta-\eta_{sat})/(\eta_{init}-\eta_{sat}))

\begin{align*}
E_{opt}(eV) & \tau_{LIC} (\text{min}) \\
\square & 1.20 \ 8.6 \times 10^4 \\
\bigcirc & 1.32 \ 5.4 \times 10^4 \\
\triangle & 1.40 \ 3.4 \times 10^4 \\
\diamond & 1.49 \ 1.0 \times 10^4 \\
\oplus & 1.58 \ 3.5 \times 10^3 \\
\end{align*}

Fig. 4.7 The degradation of the efficiency of a-SiGe single-junction solar cells with various $E_{opt}$ i-layers during light soaking (5 sun, AM-1.5 light, open circuit conditions, 25 °C), normalized by the initial and saturated values, plotted against the light-soaking time. The solid lines are fitting curves, where n=2 in Eq. (4.5) was assumed.
Degradation conditions:
5 sun with R65 filter, 48°C, open circuit

\[ E_{\text{opt}} = 1.32 \text{eV} \]

Fig. 4.8 The degradation of the efficiency of a-SiGe single-junction cells with constant \( E_{\text{opt}} \) during red light soaking (5 sun, AM-1.5 light through R65 optical filter with open circuit conditions at 25 °C), normalized by the initial (\( \eta_{\text{init}} \)) and saturated (\( \eta_{\text{sat}} \)) values. The solid lines are the fitting curves of Eq. (4.5).
Recovery conditions:
dark, 70-150°C, open circuit

Fig. 4.9 The recovery of the efficiency of a-SiGe single-junction solar cells with various $E_{\text{opt}}$ i-layers during annealing (in dark, open circuit conditions at 70, 110 and 150 °C), by the initial and saturated values of annealing, plotted against the annealing time. $\eta_{\text{b.a.}}$ and $\eta_{\text{a.a.}}$ are the efficiency before annealing and the saturated efficiency after annealing, respectively. $\eta_{\text{a.a.}}$ for 70 °C was estimated from curve fitting by Eq. (4.5).
before and after 300 minutes of annealing at 70, 110 and 150 °C, plotted against annealing time. At higher temperatures, efficiency recovers more rapidly. At a certain temperature, however, no variation in time-dependence data was observed among samples with different $E_{opt}$.

The time constants for degradation and annealing were evaluated for various $E_{opt}$ and annealing temperatures by fitting the time-dependence data from Figs. 4.7 and 4.9 to Eq. (4.5). The solid lines in Figs. 4.7 and 4.9 are fitting curves. Figure 4.10 shows the time constant for degradation during 5 sun light soaking at 25°C ($\tau_{LIC}$), and the time constant for annealing in dark ($\tau_{TIA}$) at various temperatures plotted against $E_{opt}$. $\tau_{TIA}$ becomes smaller with the increase in annealing temperature for each $E_{opt}$. This results in an increase in the annealing velocity, $1/\tau_{TIA}$, which is a thermally activated factor. It is possible to see that $\tau_{TIA}$ does not depend on $E_{opt}$, in contrast to the negative dependence of $\tau_{LIC}$ on $E_{opt}$. The activation energy for the annealing of metastable defects ($\Delta E_a$) was evaluated using an Arrhenius plot of the temperature dependence data of $\tau_{TIA}$. Figure 4.11 shows $\Delta E_a$ as a function of $E_{opt}$. $\Delta E_a$ is also not strongly dependent on $E_{opt}$.

4.4.4 Discussions

In this section, the origin of the $E_{opt}$ effects on the time constants ($\tau_{LIC}$ and $\tau_{TIA}$) is discussed. According to Eqs. (4.3) and (4.4), $\tau$ and the $N_{sat}$ are, respectively, represented as,

$$\tau \propto \{(C_1+C_2)R + \nu_1 + \nu_2\}^{-1}, \quad (4.6)$$

$$N_{sat} \propto (C_1R + \nu_1)/\{(C_1+C_2)R + \nu_1 + \nu_2\}. \quad (4.7)$$

In a light-soaking experiment at room temperature, TIC and TIA were not significant compared with LIC and LIA. Therefore, the time constant for light-induced degradation, $\tau_{LIC}$, becomes,

$$\tau_{LIC} \propto \{(C_1+C_2)R\}^{-1}. \quad (4.8)$$

On the other hand, in an annealing experiment in the dark, $R\sim 0$. Therefore, the time constant for annealing, $\tau_{TIA}$, becomes,
Fig. 4.10  The time constant for degradation during 5 sun light soaking at 25°C (τ_LIC) and annealing in dark at various temperatures (τ_TIA) plotted against $E_{opt}$. 
Fig. 4.11 The activation energy for the annealing of metastable defects, evaluated by an Arrhenius plot, as a function of $E_{\text{opt}}$. The dashed and solid lines indicate a linear fitting line and slope=1, respectively.
In Eqs. (4.8) and (4.9), it is possible to see that $\tau_{\text{LIC}}$ is determined only by the light-induced factors, $C_1$ and $C_2$, and $\tau_{\text{TIA}}$ only by the thermally-induced factors, $\nu_1$ and $\nu_2$ (Fig. 4.12).

The increase in $\tau_{\text{LIC}}$ with the decrease in $E_{\text{opt}}$, as shown in Fig. 4.10, results in the decrease of the light-induced factors, $C_1$ and $C_2$. It has already been confirmed that the $E_{\text{opt}}$ dependence of $\tau_{\text{LIC}}$ is not due to the variations in the compositions, such as $C_H$ or $C_{\text{Ge}}$, but the variations in $E_{\text{opt}}$ itself, as mentioned in 4.4.2. Figure 4.13 shows an energy-configuration diagram representing the metastability of a-Si:H alloys. The deeper and shallower minima indicate the annealed and light-soaked (defect) states, respectively. The upward arrows in the figure show the energies arising from the nonradiative recombination of hole-electron pairs, which is a driving force of the light-induced processes. The most possible explanation for the suppression of the light-induced processes in cells with a narrower $E_{\text{opt}}$ is a decrease in the recombination energy as shown in Fig. 4.13, which means the diminished energy available from hole-electron recombination for structural changes of amorphous networks. However, there is another possible cause for the $E_{\text{opt}}$ dependence of $\tau_{\text{LIC}}$. This is the change in the potential barrier between the annealed states and metastable states when $E_{\text{opt}}$ is reduced. However, the missing dependence of $\tau_{\text{TIA}}$ and of $\Delta E_a$ on $E_{\text{opt}}$, as shown in Figs. 4.10 and 4.11, rules out the participation of the barrier height or thermal annealing processes in the variation in $\tau_{\text{LIC}}$.

The decrease of defect density during annealing is thought to be due to the structural relaxation in the amorphous network via the diffusion of hydrogen atoms. Thus, the $E_{\text{opt}}$ independence of $\Delta E_a$ in Fig. 4.11 suggests that the variation of $E_{\text{opt}}$ causes little energy difference in the trap depth for hydrogen atoms, which should diffuse to remove metastable defects during annealing. This may appear strange when first considering the facts: (1) the energy level of germanium dangling bonds is shallower than that of Si dangling bonds, and (2) the binding energy of H–Ge bonds is smaller than that of H–Si bonds. However, this is consistent with previously reported results for a-SiGe:H alloys: (1) a majority of light-induced metastable defects are Si oriented despite the existence of a considerable amount of germanium oriented defects, (2) most hydrogen atoms are bonded to Si atoms, as mentioned in Chapter 3, and (3) the activation energy for hydrogen diffusion does not depend strongly on $C_{\text{Ge}}$. The activation energy of 1.2-1.3
\[ \tau = \frac{1}{(C_1 + C_2)R + v_1 + v_2} \]

**Light**  \[ \text{Light-soaking at R.T.} \]

\[
(C_1 + C_2)R \gg v_1 + v_2
\]

\[ \tau_{\text{LIC}} = \{(C_1 + C_2)R\}^{-1} \]

\[ \tau_{\text{LIC}} \uparrow \text{ when } E_{\text{opt}} \downarrow \]

**Annealing in dark**

\[ R = 0 \]

\[ \tau_{\text{TIA}} = (v_1 + v_2)^{-1} \]

Independent \( \tau_{\text{TIA}} \) of \( E_{\text{opt}} \)

**Fig. 4.12** Explanation of the \( E_{\text{opt}} \) dependence of the degradation time constant (\( \tau_{\text{LIC}} \)) and annealing time constant (\( \tau_{\text{TIA}} \)).
Fig. 4.13 An energy-configuration diagram representing the metastability of a-Si:H alloys. The upward arrows indicate recombination energies which depend on $E_{\text{opt}}$. 
eV for annealing of metastable defects in a-SiGe cells with various $E_{\text{opt}}$, as shown in Fig. 4.11, is comparable to the previously reported activation energies for hydrogen diffusion and annealing of metastable defects in a-Si:H.\textsuperscript{29-34,38}

### 4.5 Influence of optical gap on the temperature dependence of cell stability

#### 4.5.1 Temperature dependence of degradation

The degradation behavior of a-Si based solar cells is strongly affected by the temperature during light soaking. When estimating the output power of a-Si solar cells for outdoor use, the effect of temperature must be taken into account. Figures 4.14(a) and 4.14(b) show the normalized conversion efficiency of (a) a-Si single and (b) a-SiGe single cells during 5 sun, AM-1.5 light soaking at various temperatures. At room temperature, the a-SiGe single cell shows greater degradation than the a-Si single cell under continuous illumination, respectively, shown as $\times$ in Figs. 4.14(a) and 4.14(b). However, the a-SiGe cells become more stable under higher temperatures and exhibit a much greater temperature dependence compared with cells without a-SiGe i-layers. It is necessary to investigate whether this tendency explains the $E_{\text{opt}}$ dependence of activation energy for annealing metastable defects.\textsuperscript{39}

#### 4.5.2 Optical gap dependence of temperature factor

The same set of cells with various $E_{\text{opt}}$ was degraded under 5 sun light soaking at 25-75 °C. The degradation ratio in the efficiency after light soaking is defined as,

$$\Delta \gamma(t, T_{\text{LS}}) = 1 - \frac{\gamma(t, T_{\text{LS}})}{\gamma_{\text{init}}},$$

where $t, T_{\text{LS}}$ and $\gamma(t, T_{\text{LS}})$ are the light-soaking time, the temperature during light soaking and the degraded efficiency, respectively. Figures 4.15 (a) and 4.15 (b) show $\Delta \gamma(t, T_{\text{LS}})$ after (a) 1000 minutes and (b) 7500 minutes of light soaking plotted against the temperature during degradation. The solid lines in Figs. 4.15 (a) and 4.15 (b) were obtained by linear fitting. Here, the incline of $\Delta \gamma(t, T_{\text{LS}})$ against the temperature is defined as a temperature factor, $f_T(t)$. $f_T(t)$, indicating the
Fig. 4.14 The normalized efficiency of (a) a-Si and (b) a-SiGe cells during 5 sun, AM-1.5 light soaking at various temperatures.
Fig. 4.15 The degradation ratio ($\Delta \eta (t, T_{LS})$) for $t=1000$ min and (b) $t=7500$ min plotted against the temperature during light soaking.
temperature dependence of the cell stability, can be represented as follows,

\[ f_T(t) = -(d/dT_L) \Delta \gamma (t, T_L). \] (4.11)

where \( f_T(t) > 0 \) because of the negative dependence of \( \Delta \gamma \) on \( T_L \).

Figure 4.16 shows \( f_T(t) \) for 1000 and 7500 minutes of light soaking plotted against \( E_{\text{opt}} \). The temperature factor for 7500 minutes, \( f_T(7500 \text{ min}) \), has a negative dependence on \( E_{\text{opt}} \). This means that the stability of cells with a narrower \( E_{\text{opt}} \) is more strongly dependent on the degradation temperature after sufficiently long light soaking. On the other hand, the temperature factor for 1000 minutes, \( f_T(1000 \text{ min}) \), has a peaks at 1.4-1.5 eV. This is because 1000 minutes of light soaking is not sufficient for narrower \( E_{\text{opt}} \) cells to reach \( N_{\text{sat}} \) due to the slower progress of degradation, as shown in Fig. 4.7.

4.5.3 Origin of the effect of optical gap on the temperature dependence of stability

Cells with narrower \( E_{\text{opt}} \) show a stronger temperature dependence of cell efficiency after prolonged illumination (Fig. 4.16). However, it is erroneous to believe that this temperature dependence is due to the smaller activation energy for narrower \( E_{\text{opt}} \), because the independence of the activation energy for annealing from \( E_{\text{opt}} \) has already been shown in Fig. 4.11.

The \( E_{\text{opt}} \) dependence of the temperature factor \( f_T \) in Fig. 4.16 can be roughly explained using the following intuitive considerations (as shown in Fig. 4.17). Using Eqs. (4.7)-(4.9), \( N_{\text{sat}} \) can be represented as follows,

\[ N_{\text{sat}} \propto \frac{(p/ \tau_{\text{LIC}} + q/ \tau_{\text{TIA}})}{(1/ \tau_{\text{LIC}} + 1/ \tau_{\text{TIA}})}. \] (4.12)

where \( p = C_1/(C_1 + C_2) \sim 1 \), \( q = \nu_1/(\nu_1 + \nu_2) \ll 1 \), because the light-induced and thermally-induced processes are mainly the defect creation (\( C_1 \gg C_2 \)) and annealing reactions (\( \nu_1 \ll \nu_2 \)), respectively. \( N_{\text{sat}} \) is a function of both a light-induced term, \( 1/ \tau_{\text{LIC}} \), and a thermally induced term, \( 1/ \tau_{\text{TIA}} \), as shown in Eq. (4.12). When decreasing \( E_{\text{opt}} \), \( \tau_{\text{LIC}} \) increases while \( \tau_{\text{TIA}} \) remains constant as shown in Fig. 4.10. Thus, the contribution to \( N_{\text{sat}} \) of \( \tau_{\text{TIA}} \) in Eq. (4.12), which is a thermally activated factor, becomes larger. Consequently, \( N_{\text{sat}} \) for narrower \( E_{\text{opt}} \) cells exhibit...
Fig. 4.16 The factors of the temperature dependence of the degraded efficiency ($f_T(t)$) for \( t=1000 \) min and \( t=7500 \) min of light soaking plotted against $E_{\text{opt}}$. 

When $E_{\text{opt}}$ ↓ 

$f_T(7500\text{min})$ ↑
\[ \eta_{\text{sat}} \sim \log(N_{\text{sat}}) \]

\[ N_{\text{sat}} \sim \left( \frac{1}{\tau_{\text{ LIC}}} + \frac{1}{\tau_{\text{ TIA}}} \right)^{-1} \]

When \( E_{\text{opt}} \downarrow \)

- Decrease
- Constant

\[ \sim \left( \frac{1}{\tau_{\text{ LIC}}} + \frac{1}{\tau_{\text{ TIA}}} \right)^{-1} \]

Proportion of thermally activated part

Temperature dependence of \( N_{\text{sat}} \) and \( \eta_{\text{sat}} \)

Fig. 4.17 An intuitive explanation of the \( E_{\text{opt}} \) dependence of the temperature factor. (See text.)
greater temperature dependence.

This can also be demonstrated more rigorously. The negative dependence of $f_T(7500 \text{ min})$ to $E_{\text{opt}}$, as shown in Fig. 4.16, can be represented as follows, using Eq. (4.11),

\[
(d/dE_{\text{opt}})f_T(7500 \text{ min}) = -(d/dE_{\text{opt}})(d/dT) \Delta \eta (7500 \text{ min}, T_{\text{LS}}) < 0. \tag{4.13}
\]

This equality can be proven using the previous assumption. Since $\Delta \eta$ has a monotonous positive dependence to $N_{\text{sat}}$ after extended light soaking, the meaning of Eq. (4.13) is qualitatively almost equivalent to,

\[
(d/dE_{\text{opt}})(d/dT_{\text{LS}})N_{\text{sat}} > 0. \tag{4.14}
\]

This inequality has yet to be proven. When differentiating both sides of Eq. (4.12) by $T_{\text{LS}}$ and $E_{\text{opt}}$, considering that $\tau_{\text{LIC}}$ only depends on $E_{\text{opt}}$ and $\tau_{\text{TIA}}$ only on $T_{\text{LS}}$, the following relation can be obtained,

\[
(d/dE_{\text{opt}})(d/dT_{\text{LS}})N_{\text{sat}} \propto (d \tau_{\text{LIC}}/dE_{\text{opt}})(d \tau_{\text{TIA}}/dT_{\text{LS}})(p-q)(\tau_{\text{TIA}}-\tau_{\text{LIC}})/((\tau_{\text{TIA}}+\tau_{\text{LIC}})^3. \tag{4.15}
\]

Where, $d \tau_{\text{LIC}}/dE_{\text{opt}} < 0$, $d \tau_{\text{TIA}}/dT_{\text{LS}} < 0$ (see Fig. 4.10), $(p-q) \sim 1 > 0$, $(\tau_{\text{TIA}}-\tau_{\text{LIC}}) < 0$ (because the velocity of the light-induced process, $1/\tau_{\text{LIC}}$, is larger than that of the thermally-induced process, $1/\tau_{\text{TIA}}$, under conditions causing degradation), and $(\tau_{\text{LIC}}+\tau_{\text{TIA}}) > 0$. In this way, Eq. (4.14) is confirmed.

Although a-SiGe:H alloys have considerable potential for improving initial conversion efficiency, a-SiGe cells have unfortunately exhibited relatively large degradation. However, it was suggested that solar cells with a-SiGe:H offer a greater advantage for operating at high temperatures than cells with a-Si:H due to the $E_{\text{opt}}$ dependence of the defect creation process and the independence of the defect annealing process. Operating conditions should thus be considered in the design of highly-efficient solar cell submodules.
4.6 Summary

In order to reveal the effects of the i-layer $E_{\text{opt}}$ and the composition of a-SiGe solar cells on stability against light soaking, the light-induced degradation and thermally-induced recovery behavior of a-SiGe cells with a constant $E_{\text{opt}}$ and different compositions and those with various $E_{\text{opt}}$ were systematically investigated.

(1) There are at least two aspects that should be considered for stability against light exposure. One is the saturated defect density, $N_{\text{sat}}$, and the other is the degradation time constant. It was shown that compositional factors such as $C_H$ mainly affect $N_{\text{sat}}$, and $E_{\text{opt}}$ affects the time constant (Fig. 4.18).

(2) It was clearly shown that a-SiGe cells with lower $C_H$ and/or Si-H$_2$ content were more stable in a constant $E_{\text{opt}}$ system. This result confirms the contribution of incorporated hydrogen atoms on metastable defect creation. The investigation of the light-induced degradation behavior of a-SiGe:H alloys in a constant $E_{\text{opt}}$ system is significant, not only for improving the performance of these alloys themselves, but also for verifying the kinetic models proposed for a-Si materials.

(3) a-SiGe solar cells with a narrower $E_{\text{opt}}$ degrade more slowly than, but recover as fast as, cells with a wider $E_{\text{opt}}$. This is because light-induced processes, such as LIC and LIA, are suppressed in materials with a narrower $E_{\text{opt}}$, while thermally-induced processes, such as TIC and TIA, do not depend on $E_{\text{opt}}$.

(4) Both the time constant ($\tau_{\text{TIA}}$) and the activation energy ($\Delta E_a$) for thermal annealing of metastable defects do not depend strongly on $E_{\text{opt}}$. These results suggest that the variation of $E_{\text{opt}}$ causes little energetic difference in the trap depth preventing hydrogen diffusion for removing metastable defects during network relaxation by annealing, and indirectly reconfirm the suppression of the light-induced defect creation process in narrower $E_{\text{opt}}$ alloys due to the smaller recombination energy.

(5) The degree of degradation for narrower $E_{\text{opt}}$ cells exhibits a greater temperature dependence after sufficient long time light-soaking. This suggests that the saturated defect density, $N_{\text{sat}}$, which is determined by the balance of light induced and thermally-induced processes, depends on the temperature more strongly for narrower $E_{\text{opt}}$ alloys. Because, when $E_{\text{opt}}$ is decreased the contribution of the thermally activated factor to $N_{\text{sat}}$ becomes relatively larger due to the $E_{\text{opt}}$
Fig. 4.18  Effects of $E_{\text{opt}}$ and compositions of a-SiGe:H on stability against light-soaking. Compositional factors such as $C_H$ mainly affect $N_{\text{sat}}$, and $E_{\text{opt}}$ affects the time constant.
dependence of the light-induced defect creation process and the $E_{\text{opt}}$ independence of the thermally-induced annealing process. Operating conditions should thus be considered in the design of highly-efficient solar cell submodules.
References


28. \( n = \log \left( \frac{N_{\text{sat}}}{N_{\text{init}}} \right) = 2 \) in Eq. (4.5) was assumed for the fitting of degradation data in Fig. 4.7. On the other hand, \( n = 1 \) was assumed for the fitting of annealing data in Fig. 4.9, because the 1000-minute light soaking, carried out before annealing, was not sufficient to reach \( N_{\text{sat}} \).


5.1 Background

Multi-junction structures using a-SiGe:H alloys as the bottom photovoltaic materials are the most candidate of a-Si solar cells in outdoor-use power generators. In this chapter, the recent progresses in the performance of a-SiGe single and a-Si/a-SiGe tandem solar cells fabricated by the author's research group are reviewed, to which the knowledge of the present study was applied in the material design.

5.2 New concept of band-gap tailoring for a-SiGe:H i-layers

In a-Si based p-i-n solar cells, holes are the limiting carriers of the device performance. It has been, thus, generally considered that the improvement in the hole transportation is important in designing a-SiGe solar cells in which the hole mobility is smaller than in a-Si:H cells. Figure 5.1 shows the band diagram for the i-layer of previous conventional a-SiGe solar cells.\(^1\)\(^2\) \(E_{\text{opt}}\) is continuously graded in the direction of the film thickness, and the narrowest \(E_{\text{opt}}\) portion is arranged near the p-layer. This is so-called "double graded structure (DGS)" and can be fabricated by varying GeH\(_4\) flow ratio during deposition. DGS was developed to efficiently correct holes arising in the deep portion of the i-layer, in exchange for a little sacrifice in the electron transportation, by enhancing the field slope in the valence band and simultaneously by relieving the band off-sets between doped layers and i-layer.\(^1\)\(^2\) Many research groups, have been focused their efforts to optimizing the DGS for a long time.\(^1\)\(^5\) However, they faced to a dilemma. Although, in order to improve the stability it was demanded to reduce the i-layer thickness of \(\sim 300\) nm, narrowing \(E_{\text{opt}}\) by adding more Ge to keep the photon absorption drastically deteriorated the collection efficiency of carriers.

In 1992, the author's group arrived at an alternative conclusion, called "strong field structure
Incident light

Fig. 5.1. The band diagram of an a-SiGe DGS (double graded structure) cell under $I_{sc}$ condition.

Incident light

Fig. 5.2. The band diagram of an a-SiGe SFS (strong field structure) cell under $I_{sc}$ condition.
The design concepts of SFS were as follows; (1) The thickness of the i-layer was reduced to \(\sim 100\) nm to enhance the internal electric field, while remaining the minimum graded portions of p/i and i/n interfaces to relieve the off-set effects. (2) It was found that the electronic properties of a-SiGe:H show drastic deterioration with \(C_{\text{Ge}}\) over \(\sim 40\) at.\%\(.7-8\) Thus, the very narrowest \(E_{\text{opt}}\) within a critical value was carefully chosen, and the region was thickened to \(60-100\) nm to maintain a photocurrent with a thinner i-layer. SFS solved the dilemma of DGS and realized a very high collection efficiency after light-induced degradation.\(6\) From the viewpoint of the productivity in manufacturing, also SFS seems to excel DGS because the thinner i-layer can reduce the process time for deposition.

SFS also changed the status of material design for a-SiGe:H alloys. The cell performance of DGS was considered to be more sensitive to the band profiles rather than to the material properties of the narrowest \(E_{\text{opt}}\) region, because its proportion was relatively small. Besides, it was practically difficult to optimize the properties of whole region of i layer with variety of compositions. In contrary, the greater part of i layer of SFS is occupied by the narrowest \(E_{\text{opt}}\) region. Furthermore, the device performances became possible to be directly connected to the characteristics of bulk films as described in Chapters 2-4. Therefore, the properties of the narrowest \(E_{\text{opt}}\) a-SiGe:H became significantly important for SFS. These are other aspects of the background of the present study.

5.3 Material design for efficient solar cells and modules

5.3.1 A concept for optimizing i-layer compositions

The criteria for optimizing compositions of a-SiGe:H with a constant \(E_{\text{opt}}\), concluded in Chapter 2, was applied to the i-layer material design of SFS cells. Figure 5.3 schematically illustrates the initial performance, stability and stabilized performance of a-SiGe solar cells with a constant \(E_{\text{opt}}\) as functions of \(C_{\text{H}}\) of the i layer. An optimum \(C_{\text{H}}\) exists for the initial state, while the stability against light exposure has an inverse relationship with \(C_{\text{H}}\). Consequently, the best composition for the stabilized efficiency, which can be represented as the product of the initial performance and stability, slightly shifts to the lower \(C_{\text{H}}\) region than that for the initial state.
Fig. 5.3. Schematic illustrations of the initial performance, stability and stabilized performance of a-SiGe solar cells with constant $E_{\text{opt}}$ as functions of $C_H$ of the i layer. An optimum composition slightly shifts to the lower $C_H$ region than that for the initial state.
5.3.2 a-SiGe single- and a-Si/a-SiGe tandem cells

Based on this concept, efficient a-SiGe single- and a-Si/a-SiGe tandem solar cells (area: 1 cm²) were designed. a-SiGe single and a-Si/a-SiGe tandem cells consisted of TCO/ p(a-SiC:H)/ i(a-SiGe:H)/ n(a-Si:H)/ metal, and TCO/ p(a-SiC:H)/ i(a-Si:H)/ p(a-SiC:H)/ i(a-SiGe:H)/ n(a-Si:H)/ metal, respectively. The thickness and $E_{\text{opt}}$ of the a-SiGe:H i-layers are 130 nm and 1.32 eV, and those of the top a-Si:H i-layer of the tandem cell are 150 nm and 1.57 eV, respectively.

Figure 5.4 shows the initial and stabilized conversion efficiencies of an a-SiGe single-junction solar cell under red light (1 sun AM-1.5 through R65 optical filter) plotted against $C_H$ of a-SiGe:H layer. The R65 filter was selected to evaluate a-SiGe solar cells under similar conditions to the bottom of tandem cells. The light-irradiation conditions for stabilization were AM-1.5, 5 sun light through a red optical filter (R65) at 48 °C for 6 hours with the open circuit condition. Figures 5.5 shows the initial and stabilized conversion efficiencies of an a-Si/a-SiGe tandem solar cell under 1 sun AM-1.5 light plotted against $C_H$ of a-SiGe:H layer. The light-irradiation conditions for stabilization were AM-1.5, 5 sun light at 48 °C for 6 hours with the open circuit condition. These stabilizing conditions were corresponding to the one-year outdoor use. The shifts of optimum compositions for a-SiGe single- and a-Si/a-SiGe tandem solar cells agree well, as shown in Figs 5.4 and 5.5. Figures 5.6 (a) and 5.6 (b) show the efficiencies after prolonged illumination normalized by the initial values of (a) an a-SiGe single, and (b) an a-Si/a-SiGe tandem solar cells plotted against $C_H$ of a-SiGe:H layer. The incline of light-induced degradation ratios of a-SiGe single- and a-Si/a-SiGe tandem solar cells also agree well. These results in Figs. 5.4-5.6 indicate that the performance of tandem cell is very sensitive to the properties and stabilities of the a-SiGe:H bottom i-layer.

In this experiment series, very high efficiencies were achieved. Figures 5.7 (a) and 5.7 (b) show the initial and stabilized illuminated I-V characteristics of (a) an a-SiGe single-junction cell and (b) an a-Si/a-SiGe tandem cells, corresponding to the highest stabilized efficiencies. The initial conversion efficiencies of 3.7 % for the a-SiGe cell under red light and 11.6 % for the tandem cell under white light have been achieved. These efficiencies became 3.3 % and 10.6 % after intense light soaking corresponding to outdoor exposure for one year. The degradation ratio was only 8.6 %. The stabilized efficiencies for single- and tandem cells are the highest values ever reported for this size (1 cm²) of an a-Si-based solar cell.
Fig. 5.4. The initial and stabilized conversion efficiencies of an a-SiGe single-junction solar cell under red light (5 sun AM-1.5 through R65 optical filter) plotted against $C_H$ of a-SiGe:H layer.
Fig. 5.5. The initial and stabilized conversion efficiencies of an a-Si/a-SiGe tandem solar cell under 1 sun AM-1.5 light plotted against $C_H$ of a-SiGe:H layer.
Conditions for stabilization:
5 sun, AM-1.5 with R65 filter, 
48°C, open circuit, 6 h

(a) a-SiGe single

(b) a-Si/a-SiGe tandem

Fig. 5.6. The efficiencies after prolonged illumination normalized by the initial values of (a) an a-SiGe single, and (b) an a-Si/a-SiGe tandem solar cells plotted against $C_H$ of a-SiGe:H layer.
Fig. 5.7. The illuminated I-V characteristics of (a) an a-SiGe single-junction solar cell and (b) an a-Si/a-SiGe tandem solar cell before and after intense light soaking. The stabilized efficiencies for single- and tandem cells are the world's highest values ever reported for this size (1 cm²) of an a-Si-based solar cell.
5.3.3 a-Si/a-SiGe tandem submodule

The cell design techniques shown above were extended to the fabrication of larger-scale superstrate submodules (Fig. 5.8) combining with other technologies, such as a uniform deposition of thin film layers, a high-resolution laser patterning and an optimized module structure. Especially, the bottom a-SiGe:H i-layers were deposited at a relatively low temperature, ~200°C, from very highly H₂ diluted source gases (SiH₄ + GeH₄) in order to relieve the thermal damage to under-lying layers. Although the H₂ dilution method is effective to reduce Si-H₂ bonds instead of increasing process temperatures, higher-ratios of dilution are required for a-SiGe:H than that for a-Si:H, as mentioned in Chapter 4. Figure 5.9 shows the illuminated I-V characteristics of an a-Si/a-SiGe tandem submodule (area: 30×40 cm²), before and after light soaking. The world's highest stabilized efficiency of 9.5% has been achieved. The light-soaking test and measurements were performed and authorized by JQA (Japan Quality Assurance Organization).

5.4 Future prospects for industrialization

In this way, the performance of solar cells containing a-SiGe:H layers has been progressing. Although the stabilization test of JQA standard by intense light soaking was carried out at 48°C, the surface temperature of outside roof panels practically elevates to 70-80°C in summer. It was shown that the advantage in the stability of a-SiGe cells against a-Si cells are more conspicuous at higher temperatures as was discussed in Chapter 4. The feasibility of a-SiGe:H is, thus, more than the value of the authorized stabilized efficiency.

The "Fundamental Principles of Renewable Energy Introduction" was approved as drafted by the Diet in 1994, in which 4600 MW photovoltaic systems are planning to be totally installed by 2010. The target was revised upward to 5000 MW in 1998. In order to achieve the goal, it is necessary to introduce considerable amount of thin film solar cells in addition to the conventional c-Si or poly-Si, because Si wafers are running short. Now, the author's group in Sanyo is developing larger-scale a-Si/a-SiGe tandem submodules (60×90 cm²) for superstrate monolithic solar panels, and is planning to ship them on trial for outdoor use in 1999. Other companies in Japan and the US, also announced to market solar cell products using a-SiGe:H alloys. The a-Si/a-
Fig. 5.8. The outlook photograph of an a-Si/a-SiGe tandem superstrate submodule.
Fig. 5.9. The illuminated I-V characteristics of an a-Si/a-SiGe tandem superstrate submodule before and after intense light soaking. The stabilized efficiency of 9.5% is the world's highest value for this size (1200 cm²) of an superstrate-type a-Si solar submodule.
SiGe tandem is the nearest thin film solar cells to take the place of the c-/poly-Si as commercial products.

5.5 Summary

The knowledge of the present study, described in Chapters 2-4, was applied to the a-SiGe:H material design for high-efficiency solar cells and modules. The world's highest stabilized efficiency of 3.3% for an a-SiGe single junction solar cell ($1 \text{ cm}^2$) was achieved under R65 filtered light. Using this a-SiGe cell as the bottom, the world's highest stabilized efficiencies of 10.6% for an a-Si/a-SiGe tandem cell ($1 \text{ cm}^2$) was also achieved. Furthermore, the world's highest stabilized efficiencies of 9.5% for an a-Si/a-SiGe superstrate submodule ($30 \times 40 \text{ cm}^2$) was achieved by combining the cell design technique with some other technologies.
References

9. Our stabilization conditions have been confirmed to be equivalent to the JQA standard.
10. A higher stabilized efficiency for a smaller area cell (0.25cm²) has been reported in the following reference; J. Yang and S. Guha, Appl. Phys. Lett. 61, 2917 (1992).
Chapter 6
Conclusions

In the present work, the material properties of a-SiGe:H alloys with various compositions and $E_{\text{opt}}$ were systematically investigated to unravel the difficulty as ternary alloys. The knowledge from the investigation was applied to the material design for efficient and stable solar cells. The conclusions obtained from the experimental results and considerations in the previous chapters can be drawn as follows.

6.1 Composition Dependence of Optical Gap and Other Properties of a-SiGe:H alloys

A detailed study of a-SiGe:H films deposited by a plasma-CVD method using SiH$_4$, GeH$_4$, and H$_2$ gas mixtures has been demonstrated with paying careful attention to its composition: both $C_H$ and $C_{Ge}$. Furthermore, the properties have been compared among a-SiGe:H films and solar cells with a constant optical gap of 1.32 eV and different combinations of $C_H$ and $C_{Ge}$.

(1) Concerning the correlation of film properties with deposition conditions, (a) $C_{Ge}$ depends only slightly on $T_s$ and decreases with a rise in rf power, (b) $C_H$ increases with a decrease in $T_s$ or an upturn of $R_D$, (c) the optimum $R_D$, which corresponds to the maximum photo-sensitivity, depends on $T_s$.

(2) $E_{\text{opt}}$ is controllable by changing $T_s$ and $R_D$, in addition to the [GeH$_4$/SiH$_4$] source gas mixture ratio, and can be expressed by a linear function of $C_H$ and $C_{Ge}$. As a result, films with different compositions can have the same $E_{\text{opt}}$.

(3) The optimum composition for initial properties, such as the Urbach tail characteristic energy, defect density, and conversion efficiency of solar cells, was determined for a certain $E_{\text{opt}}$ ($= 1.32$ eV). These tendencies can be explained in terms of the hydrogen bonding configuration.

(4) The optimum composition for a certain $E_{\text{opt}}$ shifts to the lower $C_H$ region after light soaking due to the larger degradation for higher $C_H$ samples. This suggests that hydrogen or Si-H$_2$ plays an important role in light-induced degradation.
6.2 Inhomogeneous Hydrogen Bonding Structures in a-SiGe:H

The composition dependence of H bonding configurations in a-SiGe:H alloy films with various compositions deposited by rf plasma CVD was systematically investigated by comparisons to a-Si:H and a-Ge:H.

(1) As $C_H$ increases from 7 to 27 at.% by varying the substrate temperature from 80 to 350°C, the normalized H content per Si atom ($C_{H(Si)}$) in a-SiGe:H drastically increases with $C_H$, while the normalized H content per Ge atom ($C_{H(Ge)}$) is almost constant at 2-4 at.% This suggests that the structural differences of a-SiGe:H with $C_H$ are mainly caused in the regions around Si atoms.

(2) When focusing on H–Si bonds, $[\text{Si–H}_2]/[\text{Si–H}]$-$C_{H(Si)}$ correlations in a-SiGe:H deposited from both low- and high- diluted source gases are equivalent with those in a-Si:H. This suggests that the construction mechanism of H bonding structures around Si atoms in a-SiGe:H is similar to that in a-Si:H.

(3) As $C_{Ge}$ increases from 0 to 60 at.% at a constant substrate temperature of 230°C, only $C_{H(Si)}$ increases form 10 to 14 at.%. The increase in $C_{H(Si)}$ with $C_{Ge}$ is considered to be caused by the existence of Ge atoms which prevent H-elimination reactions around Si atoms. This increase in $C_{H(Si)}$ indirectly causes an increase in $[\text{Si–H}_2]/[\text{Si–H}]$ and a material deterioration by alloying.

(4) The preferential attachment coefficient, $P = C_{H(Ge)}/C_{H(Si)}$, has positive correlations to both $C_H$ and $C_{Ge}$. The $P$ value is considered to be determined not simply by the statistical difference of the bonding probabilities of H to Si and to Ge, but by the kinetics of H elimination during film growth. The $C_{H(Ge)}$ value is supposed to be solubility limited, while the $C_{H(Si)}$ value is surface reaction limited.

(5) Two random models were proposed to describe the construction kinetics of H–Si bonding structures, and these models were compared to the experimental results. H-bonding configurations of high-diluted samples are almost random. On the other hand, H-bonding configurations of low-diluted samples are not random but selectively contains polyhydride bonds.
6.3 Effects of i-layer Optical Gap and Compositions on a-SiGe Solar Cell Stability

In order to reveal the effects of i-layer $E_{\text{opt}}$ and the composition of a-SiGe solar cells on stability against light soaking, the light-induced degradation and thermally-induced recovery behaviors of a-SiGe cells with a constant $E_{\text{opt}}$ and different compositions and those with various $E_{\text{opt}}$ were systematically investigated.

(1) There are at least two aspects that should be considered for stability against light exposure. One is the saturated defect density, $N_{\text{sat}}$, and the other is the degradation time constant. It was shown that compositional factors such as $C_H$ mainly affect $N_{\text{sat}}$, and $E_{\text{opt}}$ affects the time constant.

(2) It was clearly shown that a-SiGe cells with lower $C_H$ and/or Si-H$_2$ content were more stable in a constant $E_{\text{opt}}$ system. This result confirms the contribution of incorporated hydrogen atoms on metastable defect creation. The investigation of the light-induced degradation behavior of a-SiGe:H alloys in a constant $E_{\text{opt}}$ system is significant, not only for improving the performance of these alloys themselves, but also for verifying the kinetic models proposed for a-Si materials.

(3) a-SiGe solar cells with a narrower $E_{\text{opt}}$ degrade more slowly than, but recover as fast as, cells with a wider $E_{\text{opt}}$. This is because light-induced processes, such as LIC and LIA, are suppressed in materials with a narrower $E_{\text{opt}}$, while thermally-induced processes, such as TIC and TIA, do not depend on $E_{\text{opt}}$.

(4) Both the time constant ($\tau_{\text{TIA}}$) and the activation energy ($\Delta E_a$) for thermal annealing of metastable defects do not depend strongly on $E_{\text{opt}}$. These results suggest that the variation of $E_{\text{opt}}$ causes little energetic difference in the trap depth preventing hydrogen diffusion for removing metastable defects during network relaxation by annealing, and indirectly reconfirm the suppression of the light-induced defect creation process in narrower $E_{\text{opt}}$ alloys due to the smaller recombination energy.

(5) The degree of degradation for narrower $E_{\text{opt}}$ cells exhibits a greater temperature dependence after sufficient long time light soaking. This suggests that the saturated defect density, $N_{\text{sat}}$, which is determined by the balance of light-induced and thermally-induced processes, depends on the temperature more strongly for the narrower $E_{\text{opt}}$ alloys. Because, when $E_{\text{opt}}$ is decreased the contribution of the thermally activated factor to $N_{\text{sat}}$ becomes relatively larger due to the $E_{\text{opt}}$ dependence of the light-induced defect creation process and the $E_{\text{opt}}$ independence of the thermally...
induced annealing process. Operating conditions should thus be considered in the design of highly-efficient solar cell submodules.

6.4 Applications to Efficient and Stable Solar Cells

The knowledge of the present study, described in Chapters 2-4, was applied to the a-SiGe:H material design for high efficiency solar cells and modules. The world’s highest stabilized efficiency of 3.3% for an a-SiGe single junction solar cell (1 cm²) was achieved under R65 filtered light. Using this a-SiGe cell as the bottom, the world's highest stabilized efficiencies of 10.6% for an a-Si/a-SiGe tandem cell (1 cm²) was also achieved. Furthermore, the world’s highest stabilized efficiencies of 9.5% for an a-Si/a-SiGe superstrate submodule (30 × 40 cm²) was achieved by combining the cell design technique with some other technologies.

6.5 Suggestions for Future Works

Very high stabilized efficiencies for a-Si/a-SiGe tandem cells and modules were achieved through the present work. These performances are already at a feasible level for outdoor commercial products such as PV roof panels.

The next step for industrialization is further reduction of the production cost. Improvements in the through-put of the i-layer deposition process and in the utilization of GeH₄ source gas (which is much more expensive than SiH₄) will be effective in reducing the depreciation of CVD equipment and the direct material cost, respectively. These targets conflict with the previous guiding principles for high-quality a-Si:H deposition, in which large amounts of source gas flow and low rf power density were recommended. Therefore, study of the high deposition-rate (R₉) process under source-gas depletion conditions becomes important. An alternative to rf plasma CVD, VHF plasma¹ or Hot-Wire CVD²,³ which achieved high R₉ of high-quality a-Si:H might be also useful for a-SiGe:H.

Another area that needs to be investigated is the nature of unstable a-Si related materials. In this
thesis, the effect of hydrogen on light-induced degradation were clearly abstracted by using a-
SiGe:H alloys with a constant $E_{\text{opt}}$ and different compositions. However, the kinetics of metastable
defect creation has not yet been clarified. This is still an important issue in order to make drastic
improvements in the photo-stability of the materials.

From the point of view of material properties, an increase in the deposition temperature (which
result in low $C_H$) is an appropriate direction due to the following reasons; (a) $R_D$ can be increased
because the optimum $R_D$ becomes higher for higher process temperature (as mentioned in 2.3.2),
(b) usage of Ge can be suppressed since $E_{\text{opt}}$ is determined by the combination of $C_H$ and $C_{Ge}$ (as
mentioned in 2.4), and (c) the stability against light soaking is improved (as mentioned in 2.5.2).
However, the high-temperature ($>250 ^\circ$C) process causes thermal damage to the underlying layer
and deteriorates the p-i-n device performance.$^4$ Thus, it is of interest to reduce $C_H$ without adding
thermal energy, or to develop thermally-stable device structures.

The author sincerely hopes that the results described in this thesis will contribute to the material
science and device technology of a-Si alloys, and to the further progress of the industrialization of
solar cells in the near future.
References


List of Publications

I. Regular Papers and Letters

1. "Film Property Control of Hydrogenated Amorphous Silicon Germanium for Solar Cells"


2. "Optimization of a-SiGe:H Alloy Composition for Stable Solar Cells"


4. "Effect of the i-Layer Optical Gap on the Light-Induced Degradation of a-SiGe Solar Cells"


7. "Composition Dependence of Local H Bonding Structures in a-SiGe:H Deposited by RF Plasma CVD"

    Akira Terakawa and Hiroyuki Matsunami, submitted to be published.
8. "Random Models Describing the Construction Mechanism of Hydrogen-Silicon bonds in Hydrogenated Amorphous Silicon"

Akira Terakawa and Hiroyuki Matsunami, in preparation.

9. "Control of a-SiGe:H Film Quality with Regard of Their Composition"


10. "Approaches for Stable Multi-Junction a-Si Solar Cells"


11. "Effects of High Hydrogen Dilution at Low Temperature on the Thin Film Properties of Hydrogenated Amorphous Silicon Germanium"


12. "Effects of Very High Hydrogen Dilution at Low Temperature on Hydrogenated Amorphous Silicon Germanium"


II. Proceedings of International Conferences

1. "Improvement in Performance of a-SiGe:H Solar Cells For Multi-Junction Cells" (Oral)


2. "Improvement For High-Efficiency, Stable Multijunction Cells" (Oral)

3. "Control of a-SiGe:H Film Quality with Regard of Their Composition" (Oral)


4. "Hydrogenated Amorphous Silicon Germanium for Stable Solar Cells" (Oral)


5. "Approaches for Stable Multi-Junction a-Si Solar Cells" (Plenary)


7. "Effect of Hydrogen on Stability of a-SiGe:H and a-SiC:H" (Poster)


8. "The Effect of the Optical Gap and Compositions of a-SiGe:H Cells on the Time Decay of Light-Induced Degradation" (Oral)

9. "Effects of Hydrogen Dilution on a-Si/a-SiGe Tandem Solar Cells" (Poster; the best poster awarded)


10. "Effects of Very High Hydrogen Dilution at Low Temperature on Hydrogenated Amorphous Silicon Germanium" (Oral)


III. Related Papers

1. "Low-Hydrogen-Content, Stable Amorphous Silicon Thin Films Prepared by Ion-Assisted Method"


2. "Effect of Composition on the Properties of Amorphous Silicon Carbide at a Certain Optical Gap"

Biographical Note

The author was born to Makoto and Katsuko Terakawa on July 13th, 1967, in Nara City, Japan. After completing three years at Nara High School, a prefectural coeducational school in Nara City, he entered Kyoto University in 1986. There he began his studies in the field of engineering and graduated from the Department of Precise Engineering in 1990. He then joined the R&D Headquarters of Sanyo Electric Co., Ltd., with a great interest in the development of large-scale, low-cost solar cells as a clean energy source for the future.

At the New Materials Research Center (the Functional Materials Research Center until 1993) of Sanyo, he started working in the field of amorphous silicon-related materials and their applications to solar cells in 1990. He began to work with hydrogenated amorphous silicon germanium alloys in the fall of 1992. After several years of working in this field, he decided to study material science and the device physics of semiconductors at graduate school. In April 1997, he entered the Graduate School of Kyoto University to begin his Ph.D course in the Department of Electronic Science and Engineering under Professor Hiroyuki Matsunami, an authority in semiconductor physics, while continuing his research activities in Sanyo.

He is a member of the Japan Society of Applied Physics and of the Japan Society of Solar Energy.