CHAPTER I INTRODUCTION

Crystalline/crystalline semiconductor heterojunctions have been studied extensively over the years,[1-7] and their applications to devices such as heterojunction-bipolar transistors (HBT) with a wide band-gap emitter, laser diodes, and solar cells are well known. From the viewpoints of understanding the fundamental device physics, Anderson,[2] Rediker et al.,[3] Hampshire et al.,[4] Riben et al.,[5,6] Donnelly et al.,[7] and other groups reported the electrical properties of heterojunctions of crystalline materials. Anderson has initially proposed an energy-band diagram assuming no interface states and extremely abrupt change from one material to the other. Rediker et al.,[3] Hampshire et al.,[4] and Riben et al.[5] reported the experimental evidences for supporting the abrupt heterojunction model (i.e., Anderson's model) through their capacitance-voltage (C-V) measurements. With regard to the current-transport mechanism of the heterojunctions, Anderson[2] and Perlman et al.[8] have put the basis of their calculations on a Shockley diffusion model[9] and a Schottky emission model,[10] respectively, while Riben et al.,[5,6] Donnelly et al.,[7] and Rediker et al.[3] have independently published tunneling models to explain their own data.

On selecting the combination of crystalline materials in crystalline/crystalline semiconductor heterojunctions, it is always necessary to consider lattice matching between two crystalline materials, which greatly affects the properties of the heterojunctions. In the case of amorphous/crystalline semiconductor heterojunctions, on the other hand, it is not always necessary to consider the combination. Moreover, it is much easier to fabricate the heterojunctions than to do crystalline ones, for example, good amorphous films can easily be deposited onto crystalline semiconductors at such a low temperature of 250 ℃. Grigorovici[11] was the first to report the properties of amorphous germanium/crystalline germanium heterojunctions. Stourac[12] later reported that

chalcogenide/crystalline semiconductor heterojunctions could be essentially approximated by abrupt heterojunctions, and reported that the current-transport mechanism could be based on space-charge-limited currents (SCLC) in the amorphous material (chalcogenide). However, those amorphous materials were not appropriate for most of device applications. This is because the electrical properties of those amorphous materials were poor, i.e., it was quite difficult to make p-n control in these films.

In amorphous semiconductors, doping experiments intending to control the Fermi level from the conduction-band edge to the valence-band edge were not successful before 1975. In 1975, Spear and LeComber[13] achieved the initial success of p-n control in hydrogenated amorphous silicon (a-Si:H) using a glow-discharge technique, which was followed by the announcement of a-Si:H solar cells by the RCA group (Carlson and Wronski) in the following year.[14] This was recognized as real break through, because some pessimistic suggestions had been made by Mott[15] and Gubanov,[16] independently, against the capability of p-n control in disordered structures before 1975. The incorporation of hydrogen into amorphous silicon reduced the number of electrically active gap states, and thereby enabled p- or n-type doping via the incorporation of group Ⅲ or group Ⅴ element, respectively. Since then, a great number of experiments have been done in the area of a-Si:H from the viewpoints not only of the physics of amorphous semiconductors but also of their applications to a variety of electronic devices such as thin-film solar cells, xerographies, direct-contact line sensors, and thin-film transistor arrays.

Amorphous/amorphous semiconductor heterojunctions have been used for most of device applications, and for instance, hydrogenated amorphous silicon-carbon alloy ($a\text{-}Si_{1-x}C_x:H$)/a-Si:H solar cells have shown a great potentiality.[17] However, the physics of amorphous/amorphous semiconductor heterojunctions is clearly far from being understood; even the amorphous homojunctions being not yet completely understood.[18] The study of amorphous/crystalline semiconductor heterojunctions can thus be a first step towards understanding amorphous/amorphous

semiconductor junctions. From the investigation of amorphous/crystalline semiconductor heterojunctions, moreover, important information on amorphous semiconductors has been found to be obtained.[19] And this study has been important to take advantage of both the good properties of amorphous and crystalline materials in one device.[20]

In the early 1980's, it started to study hydrogenated amorphous silicon-based alloy/crystalline silicon (c-Si) heterojunctions. Sasaki et al.[21] have investigated the diodes with Al/undoped a-Si:H/n c-Si structures, and from the high-frequency C-V characteristics of them density-of-state (DOS) distributions [g(E)] in a-Si:H were estimated. From the reasons of similarity of high-frequency C-V characteristics between those heterojunctions and a metal-oxide-semiconductor (MOS) diode as well as of similarity of very high resistivity between the undoped a-Si:H film and the oxide film, it was natural to discuss their high-frequency C-V characteristics using a MOS-type analysis.

We have studied the diodes with Mg/undoped a-Si:H/p c-Si structures,[22] where the conduction type of undoped a-Si:H is n-type[23] and Mg forms a good Ohmic contact with undoped a-Si:H.[24] These diodes exhibited good rectifying properties and the current-voltage (I-V) characteristics of those diodes were found to originate from a p-n junction of the undoped a-Si:H/p c-Si heterojunction, which means that the depletion regions are formed in both sides of a-Si:H and c-Si and are changed by a dc applied voltage. Although the high-frequency C-V characteristics were somewhat similar to those of MOS diodes, they were discussed using a p-n junction-type analysis, which could estimate a midgap-state density (N_I) in undoped a-Si:H and conduction-band discontinuity (ΔE_C) between a-Si:H and c-Si. This method is referred to as a steady-state heterojunction-monitored capacitance (HMC) method.

Smid et al.[25] have also surveyed the undoped a-Si:H/p c-Si heterojunctions and concluded on the analogy of the study of chalcogenide/crystalline semiconductor heterojunctions that the currents in them were SCLC (i.e., bulk-limited currents), not

junction-limited currents which we have proposed. Moreover, the g(E) above the Fermi level in a-Si:H was estimated using an SCLC-type analysis.

As is clear from the above descriptions, two kinds of analyses have been proposed in order to explain those C-V characteristics;

1) a MOS-type analysis,

2) a p-n junction-type analysis.

Moreover, two sorts of current-transport mechanisms have been proposed in order to explain those I-V characteristics;

1) a bulk-limited current-transport mechanism,

2) a junction-limited current-transport mechanism.

Since those were reported, many researchers have been interested in those heterojunctions.

From a lot of studies in this field, the a-Si:H/c-Si heterojunction has been found to have junction properties suitable for a variety of device applications,[20] such as

(a) a high forward-to-reverse current ratio;

(b) a small dark current even at a large reverse bias condition;

(c) wide depletion regions in both a-Si:H and c-Si;

(d) large valence-band discontinuity (ΔE_V) and small conduction-band discontinuity (ΔE_C) between a-Si:H and c-Si.

Okuda et al.[26] have reported a-Si:H/poly-crystalline silicon stacked solar cells. Rahman and Furukawa[27] have reported the electrical properties of p^+ a-$Si_{1-x}C_x$:H/n c-Si heterojunctions, and applied those heterojunctions to solar cells which showed the open-circuit voltage of 0.50 V, the short-circuit current of 30 mA/cm^2, and the efficiency of 11.38 % under AM1 light (100 mW/cm^2). Also Furukawa's group[28] has studied an HBT with a wide band-gap emitter made of hydrogenated amorphous silicon-based alloys. Ghannam et al.[29] have investigated the similar HBTs. Mimura and Hatanaka[30] have studied vidicon targets without a p-n diode array, whose main junction is a B-doped a-Si:H/n c-Si heterojunction. Yabe et al.[31] reported a gamma-ray detector with an undoped a-Si:H/p c-Si heterojunction. Vidicon targets

and gamma-ray detectors make good uses of junction properties (b) and (c), solar cells take advantage of (a) and (c), and n-p-n HBTs make good uses of (a) and (d). Another big advantage of these heterojunctions is a low-temperature fabrication process.

There have been some disputes about those experimental results. For example, we have obtained that the average value for ΔE_C between a-Si:H and c-Si is 0.20 eV,[22] indicating that the main band discontinuity occurs in the valence band ($\Delta E_V \sim 0.44$ eV). On the other hand, Cuniot and Marfaing[32] have insisted that ΔE_V is close to zero using an internal photoemission technique, while Mimura and Hatanaka[33] have obtained the results similar to ours using the same internal photoemission technique as Cuniot and Marfaing used. Essick and Cohen[34] reported that ΔE_C was nearly zero (~ 0.05 eV) using the temperature dependence of capacitance in undoped a-Si:H/n c-Si heterojunctions. Another problem is concerned with their current-transport mechanism. We have proposed a multistep-tunneling capture-emission (MTCE) current for a forward bias condition and a generation current in the depletion regions for a reverse bias condition.[20,22] Xu et al.[35] and Symons et al.[36] have supported the MTCE model, and Mimura and Hatanaka[37] successfully applied the MTCE model to B-doped a-Si:H/n c-Si and B-doped a-Si:H/n-type crystalline gallium arsenide (n c-GaAs) heterojunctions. However, Mimura and Hatanaka[38] have insisted that in the case of B-doped a-Si:H the reverse current is a generation current at the interface, not in the depletion regions.

As for the theoretical approach of amorphous/crystalline semiconductor heterojunctions, Rubinelli et al.[39] first simulated their C-V characteristics at 0 Hz. The theory of the C-V characteristics of Schottky barrier junctions with amorphous semiconductors as well as amorphous/crystalline heterojunctions has not been well developed. There are two main problems when one tries to simulate the C-V characteristics: One is how to deal with energetically distributed gap states, and the other is how to treat the frequency dependence of capacitance, which is related to the dielectric relaxation time of the highly resistive

amorphous film as well as to the trapping/detrapping time of carriers between gap states and the extended states. Because of the latter problem, almost all the models can accurately simulate only zero-frequency C-V characteristics which cannot experimentally be measured. However, it has been found that the simulation of the high-frequency C-V characteristics in highly resistive amorphous/lowly resistive crystalline heterojunctions can easily solve the latter problem as follows. Since the frequency is high enough to be able to neglect the dielectric relaxation process as well as the trapping/detrapping process in the amorphous film, one only requires the thickness of the amorphous film and the width of the depletion region in the crystalline semiconductor produced by a dc reverse bias in order to calculate the capacitance, indicating that it is able to simulate accurately the high-frequency C-V characteristics of those amorphous/crystalline semiconductor heterojunctions.

Another big subject has been how to estimate g(E) in the mobility gap of amorphous materials, as shown in Fig. 1.1, because the optoelectronic properties of a-Si:H films are critically linked with the g(E) in a-Si:H. In order to enhance the performance of a-Si:H-based devices such as solar cells and thin-film transistors where undoped a-Si:H layers play the most important role, a low g(E) in undoped a-Si:H is essential. Measurement of the g(E) and understanding of the nature of gap states are, therefore, very important. The problem has received considerable attention, and many techniques have been developed to determine the g(E). These include both optical and electrical methods. Photoacoustic spectroscopy (PAS),[40] photothermal deflection spectroscopy (PDS),[41] and constant photocurrent measurements (CPM)[42] give the variation of the optical absorption coefficient (α) versus the photon energy ($h\nu$) in the material. The number of defects is related to the absorption. However, the optical absorption coefficient is associated with a joint density of the initial and final states. Therefore, in general, it is rather difficult to distinguish one from the other. The main results obtained by PAS, PDS, and CPM are considered to show information on the valence-band tail in the

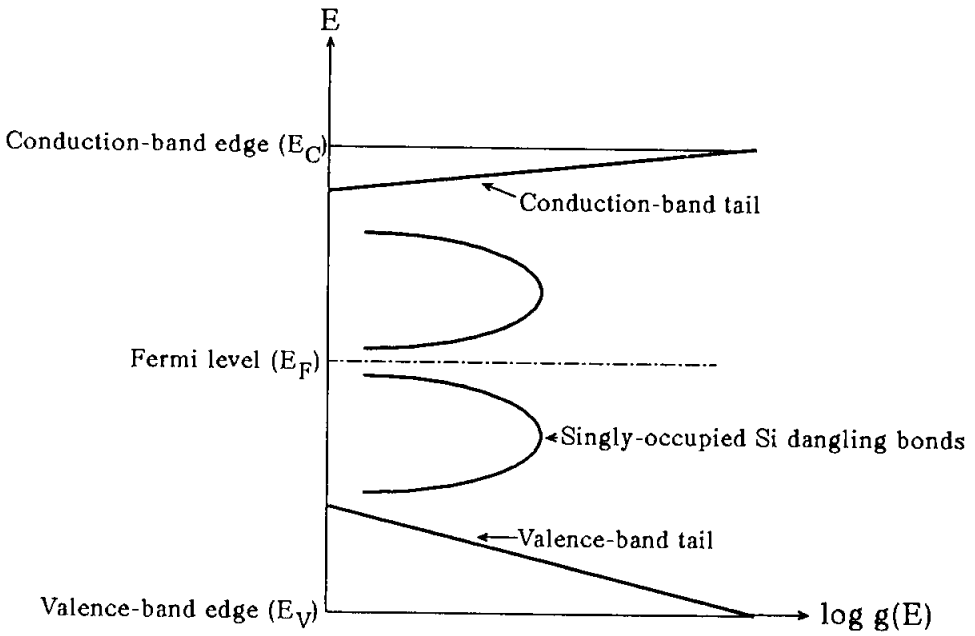

Fig.1.1. Schematic sketch of density-of-state distribution [g(E)] in undoped a-Si:H.

case of hydrogenated amorphous silicon-based alloys. While modulated photocurrent (MPC) methods[43] give information on the peak position of g(E) above the Fermi level for highly resistive (e.g., undoped) a-Si:H, estimation of the actual density of gap states is impossible. SCLC measurements[44] do give quantitative estimation of the g(E), but only above the Fermi level. However, the determination of the g(E) below the Fermi level for undoped films is important, because gap states located below the Fermi level include singly-occupied Si dangling bonds which are considered to be main midgap states. Moreover, those midgap states would determine the optoelectronic properties of the film and would, therefore, affect the performance of devices based on these films. Transient capacitance methods like deep-level transient spectroscopy (DLTS)[45] and isothermal capacitance transient spectroscopy (ICTS),[46] which usually make use of a Schottky barrier junction, are tested techniques for determining the g(E) below the Fermi level. However, these methods are limited in their application to doped samples of low resistivity. For high resistivity materials, such as undoped or compensated a-Si:H films, the dielectric relaxation times are too long for the measurement of the capacitance which can reflect the depletion width in the junction. That is why we have tried to determine the g(E) below the Fermi level in undoped hydrogenated amorphous silicon-based alloys. Since the steady-state HMC method could determine the density of the midgap states, transient capacitance of the undoped a-Si:H/p c-Si heterojunction must include information on the g(E) below the Fermi level in a-Si:H.[19,22] Actually, the study of the transient HMC has made it possible to determine the g(E) below the Fermi level in highly resistive amorphous semiconductors.[19]

A great problem, which has been directly associated with the degradation of the efficiency of a-Si:H solar cells, was reported in 1977, that is, Staebler and Wronski[47] discovered photo-induced metastable changes in the dark conductivity and photoconductivity of undoped a-Si:H. They found that both conductivities decrease after expose to prolonged band-gap illumination, and are restored to their original state by

subsequent thermal annealing at 150-200 ℃. Since then, much work has been done to elucidate the mechanism of this light-induced phenomenon, commonly called the Staebler-Wronski (S-W) effect, because it is directly associated with the stability of amorphous silicon-based photosensitive devices. Stutzmann et al.[48] have proposed the following mechanism; the rate of increase in dangling bond density (N_s) determined by electron spin resonance (ESR) measurements is given by the relation that dN_s/dt is proportional to $\Delta n \Delta p$, where Δn and Δp are the free electron and hole concentrations, respectively, under light exposure. Each concentration is proportional to G/N_s, where G is the carrier generation rate by light exposure. They have concluded that $N_s(t)$ is proportional to $G^{2/3}t^{1/3}$, where t is the time of light exposure. Once N_s has been increased by light exposure, the kinetics of its thermal annealing can be explored. Stutzmann et al.[49] have proposed a monomolecular annealing process with a distribution of activation energies (E_a), while Lee et al.[50] have proposed a bimolecular annealing process with constant E_a. Smith and Wagner[51] expanded the Stutzmann's model into a more general model which can explain the reason why N_s cannot be reduced to the value below 10^{15} cm^{-3} for undoped a-Si:H. Since the transient HMC method enables us to carry out the real-time measurements of the g(E) in the process of a 150-℃ annealing,[52] the annealing kinetics can be investigated and E_a at each energy position of midgap states can be directly determined from the method, where the g(E) can be obtained in a short time (e.g., several seconds). As is described above, both the nature and creation models of metastable midgap states have intensively been investigated.

The contribution of this thesis to a-Si:H solar cells is mentioned. As shown in Fig. 1.2, an n^+-p diode is suitable for a crystalline semiconductor solar cell while a p-i-n diode is desirable for an amorphous semiconductor solar cell, which results from the difference between minority carrier diffusion lengths in crystalline and amorphous semiconductors. In the crystalline semiconductor, electrons of electron-hole pairs produced by light exposure in the bulk region of the p-layer are

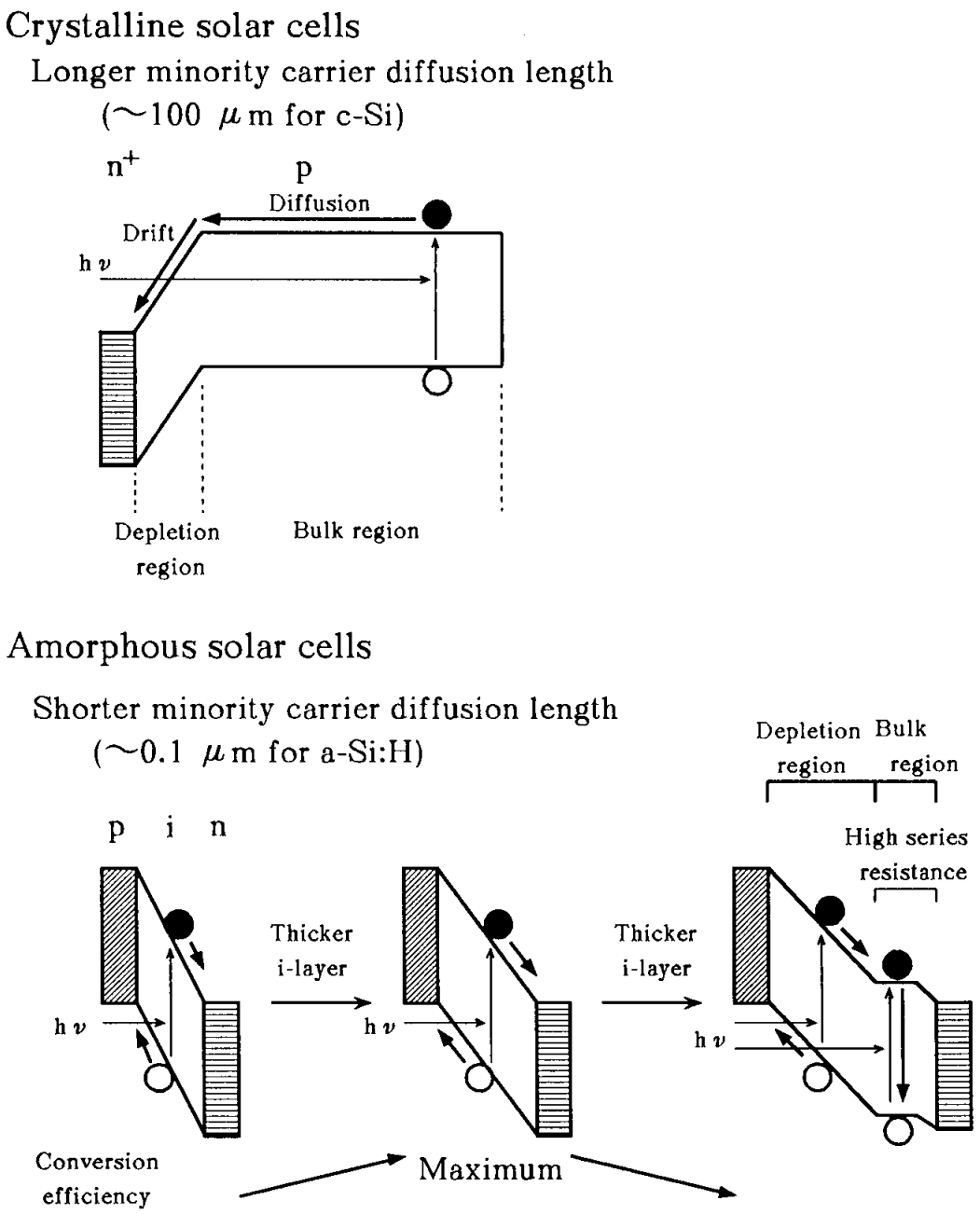

Fig.1.2. Schematic sketches of energy-band diagrams in crystalline and amorphous solar cells. The conversion efficiency of amorphous p-i-n solar cells depends on the i-layer thickness. The symbols of ○ and ● represent a hole and an electron, respectively.

diffused into the depletion region and are separated by the internal field in the depletion region, as shown in Fig. 1.2. In the amorphous semiconductor, however, electron-hole pairs cannot be separated due to its much shorter diffusion length. That is why the internal field is necessary in the place where electron-hole pairs are produced by light exposure, suggesting that the most suitable structure for the amorphous semiconductor is a p-i-n diode structure, where the i-layer is usually an undoped a-Si:H layer. Since light absorption in the i-layer contributes to a photocurrent of the a-Si:H solar cell, the thicker the i-layer becomes, the higher its conversion efficiency might be considered to be. However, a thicker i-layer is divided into the depletion region and the bulk region shown in Fig. 1.2, and the latter region does not contribute to the photocurrent at all. To make matters worse, the bulk region acts as high series resistance in the circuit, which means that the efficiency drops down. The thickest i-layer which is completely depleted, therefore, is desirable. A space-charge density (N_I) in the i-layer, which determines the depletion width in the i-layer, is necessary in order to know the desirable i-layer thickness. That is why a method for determining the value of N_I is discussed in this thesis. As mentioned before, origin of the photodegradation in a-Si:H solar cells has extremely been investigated. Even if an a-Si:H solar cell is designed to deplete the whole i-layer, after light exposure the bulk region appears in the i-layer, which makes the efficiency worse. This is because N_I in the i-layer increases by light exposure from a macroscopic point of view and because the singly-occupied Si dangling bonds are produced by light exposure from a microscopic standpoint. Since the singly-occupied Si dangling bonds are correlated with the g(E) under the Fermi level as shown in Fig. 1.1, a method for determining the g(E) under the Fermi level in the i-layer (e.g., undoped a-Si:H layer) is discussed in this thesis. Figure 1.3 shows the relationship between the contents of this thesis and problems in a-Si:H solar cells.

This thesis describes the electrical properties of a-Si:H/c-Si heterojunctions and applies these properties to estimating

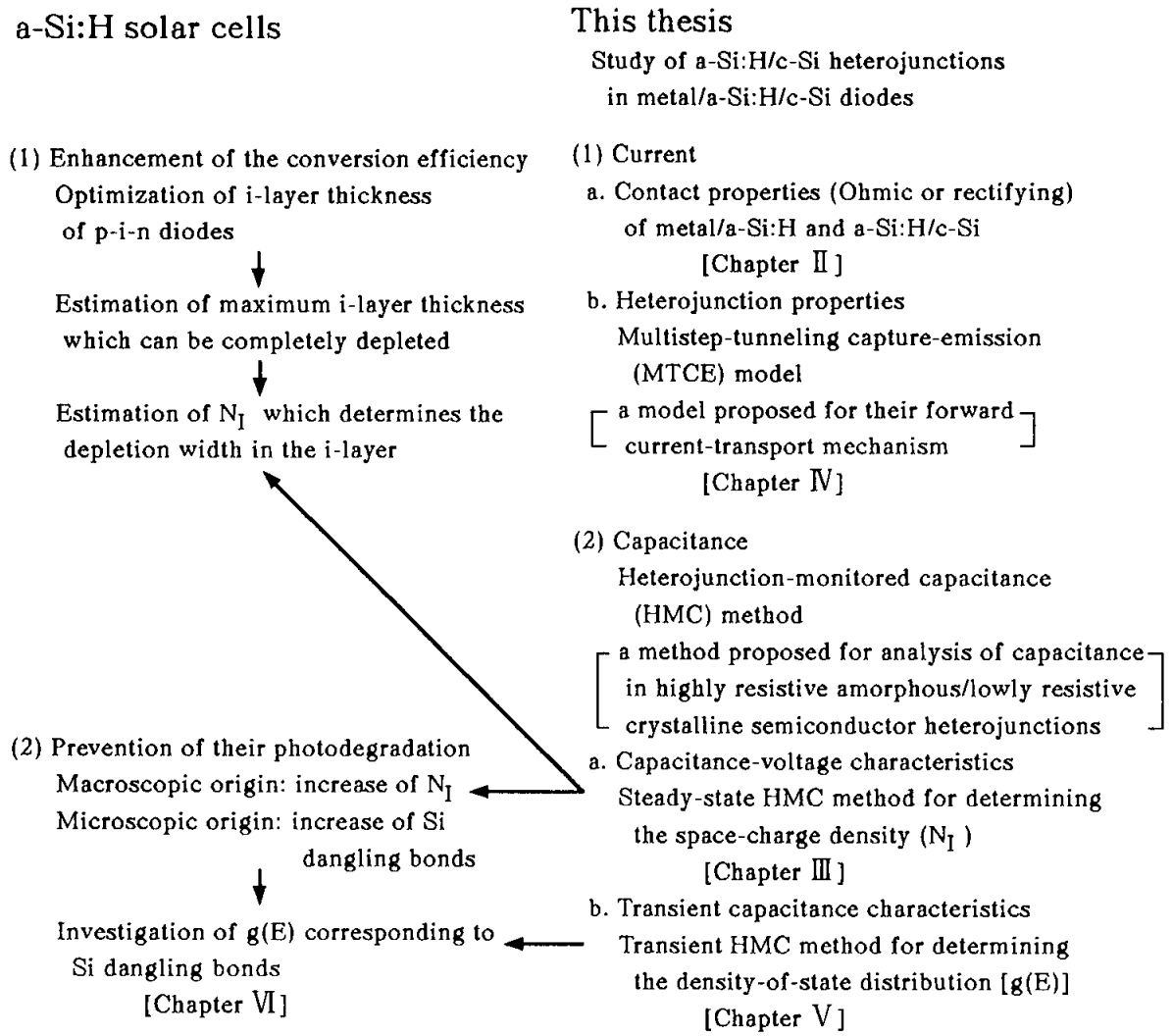

Fig.1.3. Relationship between the contents of this thesis and problems in a-SiH solar cells.

some important properties of undoped hydrogenated amorphous silicon-based alloys. Then it discusses changes of the g(E) in undoped a-Si:H by light soaking, rapid cooling, and thermal annealing.

Chapter II presents systematic experimental results of contact properties (Ohmic or rectifying) on metal/a-Si:H contacts and c-Si/a-Si:H heterojunctions. Since this study enables us to understand where a current is limited (i.e., in a junction or in the bulk) in a device and also whose contact exhibits a rectifying property, the investigation of metal/amorphous/crystalline diodes mentioned in the following chapters can be easily done.

Chapter III describes the high-frequency C-V characteristics of highly resistive amorphous/lowly resistive crystalline semiconductor heterojunctions experimentally as well as theoretically. From the study, a new method for estimating both the density of midgap states and band discontinuity between amorphous and crystalline semiconductors is developed.

Chapter IV presents the I-V characteristics of undoped a-Si:H/p c-Si heterojunctions with various resistivities of c-Si. A model for explaining the experimental results is discussed.

Chapter V develops a new method for determining the g(E) below the Fermi level in highly resistive semiconductors using the transient capacitance of these heterojunctions at various temperatures under high frequency.

Chapter VI describes the g(E) below the Fermi level in undoped a-Si:H, undoped a-$Si_{1-x}Ge_x$:H, and undoped a-$Si_{1-x}C_x$:H. Then, it discusses changes of the g(E) in undoped a-Si:H by light soaking, rapid cooling, and thermal annealing.

Finally, conclusions of the present study are made in Chapter VII.