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高效率薄膜太陽能電池之元件製作與分 析 Fabrication and analysis devices for high efficiency thin film solar cells

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摘要

目前低温矽薄膜太陽能電池的轉換效率仍然低於單晶矽太陽能電池。大部分 的轉換效率損失來自於各層塊材缺陷、介面缺陷與光致劣化現象。近幾年來,許 多研究發展高能隙的透光層(Window layer)與導電微晶矽薄膜來改善膜薄太陽 能電池的轉換效率,但是不同薄膜的不連續能隙會增加介面缺陷的影響而降低太 陽能電池的效率。在此論文裡,我們分別製作非晶矽元件與微晶矽元件,各別探 討其薄膜型太陽能電池的特性分析與薄膜缺陷狀態對於效率的影響。

對於非晶矽元件,我們希望能獲得較佳的透光層來提升非晶矽元件的效率。 因此本論文中,探討不同透光層的特性並且藉由製程來改善其元件特性。

對於微晶矽元件,我們希望能提高沉積速率並且同時保持高效率元件特性。 此外,近幾年來有相關研究指出高壓沉積方式可以達到上述目標。本論文中我們 將探討不同壓力沉積下得元件特性,並且利用不同分析方式來探討元件特性,如 利用 DLCP、QE、活化能。

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English abstract

The efficiency of low temperature silicon thin film solar cell is still lower than single crystallization solar cell. The most losses of efficiency come from the bulk trap • interface trap and light induced degradation. In recent year, most researches developed the window layer of higher energy band gap and conductive micro-Silicon to improve the efficiency of thin film. But discontinues energy gaps of different layer will increase the influence of interface trap and decrease the efficiency of solar cell. In this thesis, we fabricate respectively amorphous silicon and microcrystalline silicon thin film solar cell, and the characteristic analysis and efficiency influenced by the thin film trap state applied on thin film solar cell will be discussed.

For amorphous silicon thin film solar cell, we hope obtain greater window layer to enhance the efficiency of amorphous silicon thin film solar cell. In this thesis, we study different window layer characteristics and we also change the process parameter to improve.

We hope use high deposition rate and maintain higher cell efficiency for

microcrystalline silicon thin film solar cells. Otherwise, researches indicate that high-pressure way to achieve these goals in recent year. In this thesis, we will study device characteristics by different deposition pressure and use different analysis method such as drive level capacitance profiling (DLCP) $\$ QE $\$ and activation energy to analyze solar cells.



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Chapter 1 Introduction

1.1 Overview of solar cells technology

Photovoltaics[1] involves the direct conversion of sunlight into electricity in thin layers of material known as semiconductors with properties intermediate between those of metals and insulators. Silicon, the material of microelectronics and the information age, is the most common semiconductor. In the latter half of the 20th century, silicon photovoltaic solar cells started to be used mainly to generate small amounts of electricity in remote areas where there was no conventional source of electricity. In the 21st century, photovoltaics will grow to maturity. Almost everyone will be aware of photovoltaics since photovoltaic solar cells will be on the roof of their home or in a remote rural village.

Solar cells are the types of materials, can be amorphous silicon[2], polycrystalline silicon, and other semiconductor materials. In short, any materials which can generate electricity under illumination are found. Mainly through the different processes and methods to examine the response and light absorption and to combine a broad energy band gap, and allow short wavelength or long wavelength to be completely absorbed the revolutionary breakthrough to reduce the cost of materials.

In the past, the technology used to make most of the solar cells on crystalline-silicon wafer, fabricated so far, borrows heavily from the microelectronics industry. The silicon source material is extracted from quartz, although sand would also be a suitable material. The silicon is then refined to very high purity and melted.

However, at the upward pressure constantly of the oil price, the alternative energy source is being discussed and had a fever continuously, the solar cell industry becomes much more popular rapidly accordingly; Industry's major technology of the solar cell, in order to regard silicon as the technology of based material (Crystalline-Silicon Wafer Based) at present, but as solar cell have consumer market demand more whole it grow up fast, it can be unable to cooperate with the newly-increased solar cell demand to make the present stage produce immediately, then cause the upper reaches silicon material supply and demand lacks proper care, so solar cell manufacturers put into and rob the raw materials competition of silicon one after another. Because of silicon high demand of raw materials, silicon-based solar cell growth strength of industry restricted and contracted. Hence, known as the second generation of the thin film solar cell technology will undertake the energy with high efficiency and low cost, and substitute one of the directions.

The advantage of the thin film solar cell, which can absorb the diffusion light source, suitable for producing by a large scale, or apply to the consuming electronic product; and if there are manufacturers in the future can offer standardization of the apparatus of plating membrane and automatic production line, will make the manufacturing costs of the thin film solar cell products reduce by a wide margin. In addition, if the efficiency of silicon thin film solar cell can raise the efficiency with various parameters of optimization, so have it from the competition advantage with the crystalline silicon solar cell even more.

1.2 Motivation

The efficiency of low temperature silicon thin film solar cells is still lower than single crystallization solar cells. The most losses of efficiency come from the bulk trap \cdot interface trap and light induced degradation. In order to improve conversion efficiency of silicon thin film solar cells, and as shown in the following ways to improve; (1) improving conductivity and penetration and energy band gap of window layer[3-6] to enhance open circuit voltage and shirt circuit current; (2) depositing hydrogen microcrystalline silicon thin film[7] to decrease light induced degradation; (3) utilizing application of tandem structure to absorb spectrometry Fully; (4) adjusting p/i interface process to improve interface defects, and enhance open circuit voltage and shirt current.

In this thesis, we employed the structure of the superstrate p-i-n hydrogenated microcrystalline silicon solar cells by high rate deposition technology and to discuss solar cell performance. In addition, we also employed p-type microcrystalline silicon film (μ c – Si: B) and p-type amorphous silicon film (a – SiO: B · a – SiC: B), respectively, in p-i-n hydrogenated amorphous silicon solar cells. These devices which owned different energy band gap of window layer to investigate solar cell properties. Last, we utilized an analysis method of deep level capacitance profiling (DLCP)[8] to extract distribution of defects in the intrinsic layer, and examine film quality of the intrinsic layer for microcrystalline silicon solar cells and amorphous silicon solar cells, respectively.

Chapter 2 The principle of the solar cells

2.1 Thin Film Solar Cells Material Structure

Substrate

Thin-film solar cells devices are configured in either substrate or a superstrate structure. For superstrate configuration which is shown in Figure 2.1(a), the substrate is transparent and the contact is made by a conducting oxide coating on the substrate. For substrate configuration which is shown in Figure 2.1(b), the substrate is metal or metallic coating on a glass/polymer substrate which also acts as the contact.

Transparent conducting oxide (TCO)

Transparent conducting oxides in general are n-type degenerate semiconductors with good electrical conductivity and high transparency in the visible spectrum. Thus, a low-resistance contact to the device and transmission of most of the incident light to **1996** the absorber layer is ensured. The conductivity of a TCO depends on the carrier concentration and mobility. An increase in the carrier concentration may result in enhanced free carrier absorption, which reduces the transparency of the TCO in the higher-wavelength region. Hence increasing the mobility by improving crystalline properties is considered to be the pathway for a good TCO.[9] Besides these optoelectronic properties, the mechanical, thermal, chemical, and plasma-exposure stability and passivity[10] of TCOs are important considerations. Studies have shown[11] that only ZnO-based TCOs can withstand H-bearing plasma and are also stable up to 800K. Therefore, ZnO-based materials are being increasingly used in thin film solar cells technologies. A number of reviews on TCOs have appeared in literature.[9,12-14]

Window layer

The primary function of a window layer in a heterojunction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer; no photocurrent generation occurs in the window layer.[15] For high optical throughput with minimal resistive loss the bandgap of the window layer should be as high as possible and as thin as possible to maintain low series resistance. It is also important that any potential 'spike' in the conduction band at the heterojuction be minimized for optimal minority carrier transport. Lattice mismatch (and consequent effects) at the junction is important for consideration for epitaxial or highly oriented layers. In the case of microcrystalline layers, mismatch varies spatially and thus the complicated effect, if any, averages out.

For a-Si solar cells, depending on device configuration, the n- or p-layer is very thin and acts like a window layer that allows all the photons to be transmitted to the i-region. Given the very high absorbance of these films, a very thin doped layer (~10 nm) is required. Alloy films such as a-SiC:H having excellent optical transparency and good photoconductivity have been used as the window layers.[16]

Absorber

Amorphous, micro/nanocrystalline and polycrystalline silicon Amorphous silicon is widely accepted as a thin-film solar cell material because: (a) it is abundant and non-toxic; (b) it requires low process temperature, enabling module production on flexible and low cost substrates; (c) the technological capability for large-area deposition exists; and (d) material requirements are low, 1–2 mm, due to the inherent high absorption coefficient compared with crystalline silicon. The high absorption of light results from the inherent high disorder, dangling bonds of the order of 1019/cm³, in the material so that all optical transitions are allowed. On the other hand, the

disorder acts as recombination centers that severely reduce the carrier lifetime and pin the Fermi energy level so that the material cannot be doped either n- or p-type. Incorporation of 10% hydrogen in the film during deposition greatly reduces the density of the defects to 1016/cm³, yielding a new and exotic material, a-Si:H which has a well-defined optical threshold (mobility gap) at 1.75 eV compared with the crystalline Si indirect bandgap at 1.1 eV. The reduction in the defect density makes the a-Si:H material suitable for doping and alloying with a range of materials and for junction device fabrication. However, the properties of the material and the junction device are severely affected by the light-induced creation of metastable defects, known as the Staebler–Wronski effect. Light-induced degradation of a-Si:H devices is partially tackled by reducing the a-Si:H layer thickness so that the photogenerated carriers need to move only a short distance before they reach the electrode. However, thinning down also results in lower light absorption and thus optical confinement techniques employing diffusely reflecting front and back contacts are required to increase effective layer thickness in order to absorb the photons. Over a period of time, extensive research and development work on deposition technique and device structure have resulted in development of single-junction and multijunction devices with high efficiency and moderately good stability. The a-Si alloy materials are no longer strictly classical amorphous materials with short-range order (<1 nm). Under suitable deposition conditions and strong hydrogen dilution, nanocrystalline and microcrystalline materials^[17] are obtained. The existence of very small Si crystallites dispersed in amorphous matrix deposited by plasma enhanced chemical vapor deposition (PECVD) under high-H dilution was confirmed with infrared absorption and XRD measurements.[18] While the crystallite size and volume fraction are very small, these crystallites catalyze the crystallization of the remainder of the amorphous matrix upon annealing. Microcrystalline materials deposited by this method is found

to have less defect density and are more stable against light degradation compared with a-Si. Recently developed improved efficiency materials consist of this heterogeneous mixture of the amorphous and an intermediate range order microcrystalline material. The laser[19] and rapid thermal annealing, and optically assisted metal-induced crystallization techniques[20] were also used to obtain a microcrystalline film from an amorphous film and to increase the grain size. New high-rate deposition technologies for polycrystalline Si films and innovative solar cell designs are being evolved to make reasonably efficient cells with thickness less than 25 mm at an acceptably high throughput. For example, crystalline silicon on glass (CSG) technology combines the low manufacturing cost of thin-film technology with the established strengths of silicon wafer technology.[21] Owing to the high conductivity of the silicon, no TCO was required for the current collection. With the assistance of light trapping technique, efficient modules (as high as 7%) have been fabricated on 2-mm-thick silicon films [21] High rate deposition of poly crystalline silicon films can also by obtained by hot-wire CVD techniques.[22] Large-grain, 5–20 mm, polycrystalline silicon layers have been deposited at rates as high as 3 mm/min, using iodine vapour transport at atmospheric pressure[23]. Deposition of poly-Si for solar cell applications has been reviewed extensively in the literature.[24,25] Microcrystalline and polycrystalline silicon films have lower optical absorption in contrast to the high optical absorption in a-Si. Thus, in the former case, light trapping is necessary to extract the photon energy efficiently.

Interfaces

Thin film solar cells are comprised of several layers of different semiconductors and metals, and thus the device has a large number of interfaces. Besides these surfaces/interfaces, submicrometer grain-size polycrystalline films have a high

concentration of grain boundaries acting as internal interfaces. As far as possible, photovoltaic materials are selected to match lattice constant, electron affinity/work function and thermal expansion coefficient between the adjacent layers. However, the interface properties also get modified during device processing as a result of growth process involving the sequential deposition of multilayers at different deposition conditions. In addition, post-deposition treatments involving high-temperature annealing can alter the interface and intergrain properties. Interfacial defect states and chemical and metallurgical changes affect the optoelectronic transport properties of the device. As a result, the device parameters such as open-circuit voltage, current and fill factor can be modified significantly. Extensive scanning tunneling microscopy studies of interfaces and intergranular regions show clearly that they are not only active, but are also significantly different electronically from the bulk of the grains. On the other hand, manipulation of the interfacial structure, chemistry and metallurgy provides a powerful tool to tailor/ engineer the Fermi level, bandgap, electric field and their gradients to improve the overall device performance. Both activation and passivation of grain boundaries have been effectively used in some devices.

Amorphous Si solar cells contain a number of interfaces, particularly the p/i and n/i interfaces in the p–i–n cell structure. According to the defect pool model,[26] there is a higher defect density near the interfaces compared with the bulk of the i-region. This results in recombination processes being dependent on the position in the i-region. Improvements in the device properties by annealing under reverse bias can be explained by the movement of hydrogen to the interface and consequent reduction in the interface states.[27,28] The presence of interface states also causes open-circuit voltage limitation, particularly for the p/i interface.[29] In fact, modifying this interface by using a buffer layer increases Voc.[30] Since textured substrates are used in order to enhance the optical absorption, this affects the topography of all the layers,

depending on deposition conditions, and causes interfacial roughness.[31] The resultant optical scattering for different wavelengths can cause improvements in the photoresponse of the devices.

Back contact

For amorphous silicon devices, the back contacts are formed on n-type semiconductor (and hence higher work function metals are not required) using Ag or Al. However the use of Ag or Al directly on n-type semiconductor will result in optical losses in the long-wavelength region. The long-wavelength response of the device will be improved if the n/metal interface reflects the long-wavelength radiation back to the cell. Thus the back contact for both p–i–n and n–i–p configuration is often formed with double-layer back reflector consisting of ZnO and Ag or Al. The low index ZnO layer will effectively increase the total internal reflection from the n- ZnO interface. The optical and electrical properties of the ZnO layer play a significant role in improving the back reflection properties and also the device performance.

2.2 Parameter of Solar Cells

When the cell is exposed to the solar spectrum, a photon that has an energy less than the bandgap E_g makes no contribution to the cell output. A photon that has energy greater than E_g contributes an energy E_g to the cell output. Energy greater than E_g is wasted as heat.

In order to the power conversion efficiency of a solar cell, current -voltage (J-V) characteristics of thin film solar cells under illumination are considered, which is shown in Figure 2.2. Current-voltage characterization means determination of the basic parameters V_{oc} , J_{sc} , fill factor, and efficiency (η) which are determined by only three points on the J–V curve. While these parameters are well accepted indicators of

solar cell performance and are particularly valuable for comparing and qualifying cells, there is a wealth of additional information that can be obtained by analyzing the entire J–V curve

The open-circuit voltage, $V_{\rm oc}$, is the maximum photovoltaic that can be generated in the cell and corresponds to the voltage where current is zero under illumination. The maximum current that can run through the cell at zero applied voltage is called the short-circuit current, $I_{\rm sc}$. The shaded area in the figure is the maximum-power rectangle. Also defined in Figure 2.2 are the quantities $I_{\rm max}$ and $V_{\rm max}$ that correspond to the current and voltage, respectively, for the maximum power output

$$P_{max} = I_{max} \times V_{max}$$
The power conversion efficiency of a solar cell is given by
$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{max} \times V_{max}}{P_{in}} = \frac{I_{sc} \times V_{oc} \times F.F}{P_{in}}$$
where P_{in} is the incident power and F.F is the fill factor defined

as

 $F. F = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}}$ The fill factor is the ratio of the maximum power rectangle (shaded area) to the

The fill factor is the ratio of the maximum power rectangle (shaded area) to the rectangle of $I_{sc} \times V_{oc}$.

The essential parameter which determine the power conversion efficiency of thin film solar cell devices are the sort-circuit current (I_{sc}), the open-circuit voltage (V_{oc}), and the fill factor (F.F)

2.3 Drive-level capacitance profiling model

Drive-level capacitance profiling (DLCP) is an alternate technique for measuring the energetic and spatial distribution of defects in the band gap [8]. The DLCP method examines the junction capacitance dependence over a range of ac voltage amplitudes in addition to a range of dc bias, to obtain more information about the film response than is available from the aforementioned C-V. This technique has previously been employed to study the density of states in amorphous silicon thin films, and has greatly contributed to understanding the electronic properties of that material [32-34]. Here, we illustrate how it can also be very useful in studying microcrystalline silicon (µc-Si) films.

The frequency, temperature and band bending in the sample determine the ac junction capacitance. Only those states whose thermal emission rate r is faster than $1/\omega$ can respond during a cycle of the ac applied voltage and contribute to the measured capacitance. These states lie between the contour level E_E and the conduction band mobility edge E_C , as shown in Figure 2.3-1. This level is determined by setting $r = \omega$ to give

$$E_{\omega} = E_E(x) - E_C(x) = k_B T \ln\left(\frac{v}{\omega}\right)^{2}$$
(1)

Here k_B is the Boltzmann constant, *T* is the absolute temperature and *v* is the escape frequency ($\approx 10^{13}$ rad s⁻¹). Above this contour the filled states can equilibrate with the conduction band within the ac period; below this contour the filled states are frozen out and are unresponsive. Figure 2.3-1 also shows a characteristic length x_E where $E_E(x_E)=E_F$ is given

$$x_E = L_0 \ln \left\{ q V_0 / \left[k_B T \ln \left(\frac{v}{\omega} \right) - E_F \right] \right\}$$
⁽²⁾

where L_0 is a characteristic screening length. $V_0 = V_D - V_A$, V_D is the diffusion potential and V_A is the applied bias ($V_A < 0$ corresponds to reverse bias). For $x < x_E$, all filled states are unresponsive; for $x \ge x_E$, all states up to E_F can respond. The region $0 \le x < x_E$ functions as a dielectric with capacitance per unit area of $C_d = \varepsilon/x_E$ and ε is the dielectric constant. The region $x \ge x_E$ contributes a space charge capacitance $C_s = \varepsilon \rho_E/F_E$ where F_E and ρ_E are the electric field and charge density at x_E , respectively. These two regions constitute two capacitors in series; finally, the junction capacitance is given by

$$\frac{1}{c_d} + \frac{1}{c_s} = \frac{1}{c_j}$$

$$\Rightarrow \frac{1}{\varepsilon/x_E} + \frac{1}{\varepsilon\rho_E/F_E} = \frac{1}{c_j}$$

$$\Rightarrow C_j = \frac{\varepsilon\rho_E}{\varepsilon F_E + x_E \rho_E}$$
(3)

Equation (3) is valid for any charge or profile.

The drive-level capacitance method, which combines the temperature, frequency and dc bias dependence of the deep state response in one technique with the ac test signal amplitude (δV) as an additional independent variable, is experimentally described here. This parameter (δV) was fixed in other admittance methods and the transfer function may be assumed to be linear for such small test signals. In the case where the amplitude of the alternating voltage (δV) applied on a junction is negligible compared with the dc bias and diffusion voltage, the junction capacitance is given by equation (3). If δV is not negligible relative to the diffusion voltage it gives higher order corrections to the junction capacitance. Specifically,

$$C = C_0 + C_1 \delta V + C_2 (\delta V)^2$$
(4)

where C_0 is given by equation (3). The first-order coefficient is

$$C_1 = \frac{dC}{dV} = -\frac{\varepsilon \rho_E^2}{2(\varepsilon F_E + x_E \rho_E)^3}$$
(5)

The drive-level integrated defect state density N_{DL} is defined in terms of C_0 and C_1 as

$$N_{DL} = \frac{\rho_e}{q} = -\frac{C_0^3}{2q\epsilon A^2 C_1} \tag{6}$$

Where q is the magnitude of the elemental charge, and ε is the dielectric constant, and A is the sample area.

The coefficients C_0 and C_1 are obtained by fitting a quadratic to C versus δV ,

as shown in figure 2.3-2. To obtain the defect profile, measurements are made as a function of bias, and N_{DL} is plotted versus the depletion width (W), as shown in figure 2.3-3. The depletion width is measured from the junction.

$$W = \varepsilon A / Co \tag{7}$$

The defect density corresponds most closely to the density at the edge of the depletion width.



Chapter 3 Fabrication and measurement for amorphous silicon thin film solar cell

3.1 Experimental Procedures

In this thesis, we employed the structure of the superstrate p-i-n hydrogenated amorphous silicon solar cells, and the solar cell structure employed was glass (Asahi's textured TCO Glass)/front ZnO/p-i-n/back ZnO/Ag with an active of 0.25 cm². The device deposition condition: front ZnO contact layer was deposited ZnO:Ga with 20 nm thickness by sputter. All (a-Si:H) p, i, and n layers were subsequently deposited with very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) [3.13-17] multi-chamber system at 40 MHz. In deposition window layer (P-layer) process, the p-layer were deposited µc-Si:B and a-SiC:B and a-SiO:B thin films with 20 nm thickness at different devices, respectively. The intrinsic layer was deposited a-Si:H with 400 nm thickness. The n-layer was deposited a-Si:P with 30 nm thickness. Back ZnO contact layer was deposited ZnO:Ga with 200 nm thickness by sputter.

The solar cells were characterized by current–voltage (J–V) under standard air mass 1.5 (100mW/cm²) illuminations. The current-voltage characteristic measurement of thin film solar cell devices was performed by Agilent 4156, capacitance profiling by drive level capacitance profiling methods have been carried out by using an HP 4284A impedance meter.

3.2 Results and Discussion

Figure 3.1 shows current-voltage characteristics of amorphous silicon thin film solar cells under standard illumination conditions. These devices were varied films for window layer, and the films represent μ c-Si and a-SiC and a-SiO, respectively. We

could observe that open circuit voltage (V_{oc}) is maximum for a-SiO window layer; and is medium for a-SiC window layer; and is minimum for µc-Si window layer. However, shirt circuit current (J_{sc}) is maximum for μ c-Si window layer; and is medium for a-SiO window layer; and is minimum for a-SiC window layer. Table 3-1 summarizes the illuminated J-V parameters of a-Si:H p-i-n solar cells obtained for varied window layers. Because the value of Voc is the difference between E_{Fn} and E_{Fp} and energy band gap (E_g) which is larger could extend the difference between E_{Fn} and E_{Fp} . And energy band gap of a-SiC window layer is larger than of μ c-Si window layer. Hence, the larger E_g would obtain the larger V_{oc} for a-SiC window layer. Although the value of Jsc for a-SiC window layers is poorer than for µc-Si window layer, the whole of conversion efficiency have improve. Here the reason for J_{sc} have dropped, we deduce that this phenomenon are associated with the quality of intrinsic layers and the conductivity for window layer. Follow-up, we would make use of a technique of drive-level capacitance profiling (DLCP) measurement to examine the quality of mun intrinsic layers.

Figure 3.2(a)-3.4(a) show typical capacitance-voltage curve of the variation of junction capacitance with 100Hz for varied window layers of p-i-n a-Si solar cells at room temperature, respectively. Figure 3.2(b)-3.4(b) show N_{DL} versus depletion width for varied window layers of p-i-n a-Si solar cells at room temperature, respectively. We could observe that number of defects in the vicinity of the intrinsic layer of p/i interface were more than of bulk and i/n interface for all solar cells. We observe that number of defects for a-SiC window layer are more than for μ c-Si window layer, result in electric field of intrinsic layer for a-SiC window layer is weaker than for μ c-Si window layer, the another reason that the conductivity for a-SiC window layer is poorer than for μ c-Si window layer, then

the value of J_{sc} for a-SiC window layers is poorer than for μ c-Si window layer. In order to improve conversion efficiency further, we employ to increase electric conductivity for window layer. We adopt a-SiO material as window layer to improve J_{sc} . The result that have not only improve Jsc and Voc but also improve conversion efficiency. From DLCP analysis, We observe that number of defects for a-SiO window layer are less than for a-SiC window layer, as shown in figure 3.6. Although the value of J_{sc} for a-SiO window layer increase, it is not better than for μ c-Si window layer. The conductivity for μ c-Si window layer is lower than for a-SiO window layer after all.

Figure 3.7 show the measured values of current-voltage characteristics for a-Si thin film solar cells with temperature measurement from 25° C to 85° C under standard illumination conditions. We could observe with the value of Voc decrease as the temperature increase, as shown in figure 3.8; with the value of Jsc increase as the temperature increase, as shown in figure 3.9; with the value of conversion efficiency increase as the temperature increase, as shown in figure 3.9; with the value of .10. The first, Voc is associated with energy band gap Eg, is given by

$$eV_{oc} = E_{Fn} - E_{Fp} = E_g + kTln \left(\frac{G}{b_R N_v N_c}\right)$$

where Eg is the energy band gap

G is the generation rate b_R is the recombination rate coefficient N_V is effective density of states in the valence band N_C is effective density of states in the conduction band k is Boltzmann constant T is Kevin temperature Eg is associated with temperature, and when temperature is rise with Eg is dropped. Therefore, with the value of Voc decrease when temperature is rise. Device of µc-Si of p layer reduce the maximum amount of Voc with temperature increase to 85°C and the value about 4.63%, as shown in table 3-2. The second, Jsc is associated with collect electron-hole pairs capability. Because they generate a mass of electron-hole pairs in the intrinsic layer as temperature is rise, it can collect a mass of electron-hole pairs output abundant currents. Therefore, with the value of Jsc increase when temperature is rise. Device of µc-Si of p layer increase the maximum amount of Jsc with temperature increase to 85°C and the value about 2.94%. The last, conversion efficiency is associated with Voc and Jsc. Although with the value of Voc decrease as temperature is rise. The whole of conversion efficiency improve as temperature rise. Device of a-SiO of p layer increase the maximum amount of conversion efficiency with temperature increase to 85°C and the value about 14.8%. According to the above results, Device of a-SiO of p layer is the most sensitive to temperature.

Figure 3.11 show the measured values of current-voltage characteristics for a-Si thin film solar cells with temperature measurement from 25° C to 85° C under the condition of darkness. We could observe that current density increase as the temperature of solar cells increase for any temperature condition. Under the forward bias, we would observe change in current density rise is not the same in the voltage region of 0.1~0.5V and 0.7~0.8V and 1.2~1.3V. The characteristics of solar cells and pn diodes are the same under the condition of darkness. The current-voltage characteristics of ideal diodes are given by

$$J = J_0 \{ Exp(\frac{qV}{nKT}) - 1 \}$$
⁽¹⁾

When the ideal diffusion current dominates, n equals 1; whereas when the recombination current dominates, n equals 2. Therefore, we attempt to extract the value of n by fitting from eq. (1) in the voltage region of $0.1 \sim 0.5$ V and $0.7 \sim 0.8$ V and $1.2 \sim 1.3$ V, respectively, and shown in Table 3-3. In the voltage region of $0.1 \sim 0.5$ V and $0.7 \sim 0.8$ V and $1.2 \sim 1.3$ V, J_o also increased with increasing temperature for the cell, so temperature dependence of J_o. However, the value of n is greater than 1 for all cells. This phenomenon could be associated with series resistance effect or other factor effects. Hence, current increases more gradually with forward voltage.



Chapter 4 Fabrication and measurement for microcrystalline silicon thin film solar cell

4.1 Experimental Procedures

In this thesis, we employed the structure of the superstrate p-i-n hydrogenated microcrystalline silicon solar cells, and the solar cell structure employed was glass (Asahi's textured TCO Glass)/front ZnO/p-i-n/back ZnO/Ag with an active of 0.25 cm². The device deposition condition: front ZnO contact layer was deposited ZnO:Ga with 40nm thickness by sputter. All (μ c-Si:H) p, i, and n layers were subsequently deposited by 40 MHz in the very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) multi-chamber system. The window layer (P-layer) was deposited μ c-Si:B with 15 nm thickness. The intrinsic layer was deposited μ c-Si with 1500 nm thickness. The n-layer was deposited μ c-Si:P with 15 nm thickness. Back ZnO contact layer was deposited ZnO:Ga with 100 nm thickness by sputter. Back Silver metal layer was deposited Ag with 200 nm thickness. In VHF-PECVD process, we use a H₂ and SiH₄ gases. Application of high-rate μ c-Si:H deposition was most feasible to promote electron-impact dissociation of SiH₄ and H₂ into SiH₂ (SiH₄ + H₂ \rightarrow SiH₂). The dilution ratios R = H₂/SiH₄ were 1000/22 and 1000/14 and 1000/13 for μ c-Si:H intrinsic layer at pressures of 4Torr \sim 8Torr, respectively.

The solar cells were characterized by current–voltage (J–V) and spectral response measurements [40] under standard air mass 1.5 (100 mW/cm²) illuminations. The current-voltage characteristic measurement of thin film solar cell devices was performed by Agilent 4156, capacitance profiling by drive level capacitance profiling methods have been carried out by using an HP 4284A impedance meter. Otherwise, we make the conductivity and activation energy measurement of μ c-Si:H intrinsic layer, and measurement flow : the voltage sweep 0V to 10V and select a constant

voltage, V (mostly 10 V) is applied over the contacts and the current, I, is measured. We use equation of dark conductivity,

$$\sigma_{d} = \frac{I \times W}{V \times L \times D}$$

where I is measured current

V is applied voltage W is width of the film L is length of the film D is thickness of the film d dark conductivity. We

to find dark conductivity. We make the sample to heat from 300K to 370K for temperature measurements, and employ equation of activation energy,



4.2 Results and Discussion

Figure 4.1 shows current-voltage characteristics of microcrystalline silicon thin film solar cells under standard illumination conditions. These devices were deposited in different pressures. We could observe that short circuit current density (J_{sc}) and conversion efficiency (η) increased when deposition pressure increased, and shunt resistance (R_{sh}) and series resistance (R_s) decrease when deposition pressure increase, but open circuit voltage (V_{oc}) was almost same. Table 4-1 summarizes the illuminated J–V parameters of μ c-Si:H p–i–n solar cells obtained for varied i layer deposition rates.

Figure 4.2 shows the Quantum efficiency (QE) for several high-efficiency thin

film solar cells. Spectral response measurements are valuable to characterize the photocurrent and are commonly used to determine the losses responsible for reducing the measured short circuit current density from the maximum achievable photocurrent. QE is a dimensionless parameter given by the number of electrons which exit the device per incident photon at each wavelength. Device losses measured by QE can be optical, due to the front reflection and absorption in the window, transparent conductor, and other layers, or electronic, due to recombination losses in the absorber. We could observe that at pressures of 4 . 6Torr and pressures of 8Torr which corresponded to QE were approximately the same, respectively, in short wavelength region. Because we varied thicknesses of deposited p-type microcrystalline silicon layer, and the deposition thicknesses were thinner slightly at pressures of 8Torr than at pressures of 4 . 6Torr. They could decrease absorption losses in the thinner thickness, and could increase the number of electrons which exit the device per incident photon. Hence, the thinner thicknesses were higher QE. On the other hand, in long wavelength region, we could observe that the deposition pressure increased and QE also increased. The reason that lower deposition pressure of the thin films would deposited rate slowly, result in more oxygen go into the thin films, and oxygen could generate electron as donors when it went into the thin films, then oxygen would be trapped in the vicinity of grain boundaries.[41] Hence, the thin films resulted in tending to n⁻ quality gradually. The result that almost made built in field totally locate in the vicinity of p/i interface, and caused built in field to become weak in the vicinity of i-layer bulk and i/n interface, as shown in Figure 4.3. Because the photocurrent was proportional to built in field, the thin films of lower deposition pressure were lower photocurrent.

In order to verify high-rate deposition can decrease oxygen go into the film, we make the conductivity and activation energy measurement of μ c-Si intrinsic layer.

Figure 4.4 shows dark conductivity and photo conductivity as a function of deposition pressure. We observe that with dark conductivity and photo conductivity decrease as deposition pressure increase. It indicates obviously smaller resistance and better conductivity for low deposition pressure, and characteristic of the film is tending to n quality. Figure 4.5 shows activation energy as a function of deposition pressure. We observe that with activation energy increases as deposition pressure increases, and the value of activation energy is close to 550 meV for 8Torr deposition pressure, as shown in Table4-2. Energy band gap of µc-Si film is about 1.12eV and midgap of µc-Si film is about 550 meV, and activation energy is close to 550 meV for 8Torr deposition pressure, so Fermi level E_F of μ c-Si film is close to E_i for high deposition pressure. Yet, the value activation energy is 478 meV and Fermi level E_F of μ c-Si film is above E_i for 4Torr deposition pressure. Therefore, characteristic of µc-Si film is tending to n quality for 4Torr deposition pressure. Hence, high deposition pressure not only made characteristic of the film tending to intrinsic quality but also could Manna Manna decrease oxygen go into the film.

In brief, the thinner thicknesses of deposited p-type microcrystalline silicon layer were higher QE and independent on deposition pressures in short wavelength region; lower deposition pressure of the thin films would more oxygen go into the thin films, then the thin films made tending to n⁻ quality gradually result in almost make electric field totally locate in the vicinity of p/i interface, and the photocurrent was proportional to built in field. Therefore, the thin films of lower deposition pressure were lower photocurrent in long wavelength region.

In addition, in order to investigate about the relationship between the spatial distribution of defects in the intrinsic layer and the deposition pressure, we would make use of a technique of drive-level capacitance profiling (DLCP) for varied deposition pressures.

Figure 4.6(a)-4.8(a) show typical capacitance-voltage curve of the variation of junction capacitance with 100Hz for deposition pressures of 4-8Torr at room temperature, respectively. Figure 4.6(b)-4.8(b) show N_{DL} versus depletion width for deposition pressures of 4-8Torr at room temperature, respectively. We could observe that number of defects in the vicinity of the intrinsic layer of p/i interface were lower for higher deposition pressures; however, number of defects in the intrinsic layer of bulk and i/n interface were not any variation explicitly for arbitrarily deposition pressures, as shown in Figure 4.9. Because gas of the lower deposition pressures was less reactants than the higher deposition pressures and generated less precursors, and there had prone to plasma ion bombardment more probability in the vicinity of p/i interface, result in the destruction of the interface is very serious. Hence, it is better in the interface for higher pressure deposition. [42]

Figure 4.10 show the measured values of current-voltage characteristics for μ c-Si thin film solar cells with temperature measurement from 25°C to 85°C under the condition of darkness. We could observe that current density increase as the temperature of solar cells increase for any temperature condition. Under the forward bias, we would observe change in current density rise are different in the voltage region of 0.2V~0.4V and 0.6~1V. The characteristics of solar cells and pn diodes are the same under the condition of darkness. The current-voltage characteristics of ideal diodes are given by

$$J = J_0 \{ Exp(\frac{qV}{nKT}) - 1 \}$$
⁽¹⁾

where J_o is the saturation current density

n is the ideality factor.

When the ideal diffusion current dominates, n equals 1; whereas when the recombination current dominates, n equals 2. Therefore, we attempt to extract the

value of n by fitting from eq. (1) in the voltage region of $0.2V\sim0.4V$ and $0.6\sim1V$, respectively, and shown in Table 4-3. J_o increased with increasing temperature for all cells, and the value of n is 2 approximately for all cells in the voltage region of $0.2V\sim0.4V$. The result show temperature dependence of J_o and ideality factor n equals 2 approximately represents the quality of the recombination center. So that is recombination current dominant in the voltage region of $0.2V\sim0.4V$. In the voltage region of $0.6\sim1V$, J_o also increased with increasing temperature for all cells, so temperature dependence of J_o. However, the value of n is greater than 1 for all cells. This phenomenon is associated with series resistance effect. At low current level, the *IR* drop across the neutral regions is usually small compared to kT/q (26 mV at 300K), where I is the forward current and *R* is the series resistance. At high current level, the *IR* drop across the neutral regions is very large, and the neutral regions of i layer is huge specifically. Hence, current increases more gradually with forward voltage.

Figure 4.11 show the measured values of current-voltage characteristics for μ c-Si thin film solar cells with temperature measurement from 25 °C to 85 °C under standard illumination conditions. We could observe with the value of Voc decrease as the temperature increase, as shown in Figure 4.12; with the value of Jsc increase as the temperature increase, as shown in Figure 4.13; with the value of conversion efficiency decrease as the temperature increase, as shown in Figure 4.13; with the value of conversion efficiency decrease as the temperature increase, as shown in Figure 4.13; with the value of the first, Voc is associated with energy band gap Eg, is given by

$$eV_{oc} = E_{Fn} - E_{Fp} = E_g + kTln \left(\frac{G}{b_R N_v N_c}\right)$$

Eg is associated with temperature, and when temperature is rise with Eg is dropped. Therefore, with the value of Voc decrease when temperature is rise. Device of 4Torr deposition pressure reduce the maximum amount of Voc with temperature increase to 85°C and the value about 11.5%, as shown in table 4-4. The second, Jsc is associated with collect electron-hole pairs capability. Because they generate a mass of electron-hole pairs in the intrinsic layer as temperature is rise, it can collect a mass of electron-hole pairs output abundant currents. Therefore, with the value of Jsc increase when temperature is rise. Device of 8Torr deposition pressure increase the maximum amount of Jsc with temperature increase to 85°C and the value about 2.94%. The last, conversion efficiency is associated with Voc and Jsc. Although with the value of Jsc increase as temperature is rise, with the value of Voc decrease more than the value of Jsc increase as temperature is rise. The whole of conversion efficiency decayed as temperature rise. Device of 4Torr deposition pressure decrease the maximum amount of conversion efficiency with temperature increase to 85°C and the value about 14.8%. According to the above results, Device of a-SiO of p layer is the most sensitive to temperature.



Chapter 5 Conclusion

We succeed in introducing optimum window layer material to fabricate a-Si:H solar cells. The solar cells of window layer which used high energy band gap material would improve Voc and conversion efficiency. The window layer of a-SiO which is a kind of high energy band gap material is effective in obtaining high Voc. The maximum efficiency obtained so far is 5.75%.

In addition, we have shown that deposition pressure plays a key role in determining Jsc of μ c-Si:H solar cells fabricated using high deposition rate plasma process. High pressure deposition at 8Torr is effective in obtaining high Jsc. The maximum efficiency obtained so far is 5.045%. We propose that low oxygen concentration behavior associated with the microstructure of high pressure grown μ c-Si:H is responsible for the excellent charge collection behavior in p-i-n junction solar cells. Otherwise, we also succeed in utilizing a method technology of DLCP to extract number of detects from intrinsic layer for thin film solar cells. High deposition pressure is effective in suppressing number of detects in the vicinity of p/i interface.

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Figure



Figure 2.1(b) The type of substrate solar cells structure



Figure 2.3-1 Band diagram of p-i-n junction



Figure 2.3-3 Drive level charge density versus depletion width in the solar cell



Figure 3.1 shows current-voltage characteristics of amorphous silicon thin film solar cells under standard illumination conditions



Figure 3.2(a) Capacitance vs. dc bias for μ c-Si window layer of solar cell. The measuring frequency is 100Hz and the temperature is 300K. The amplitude of the alternating voltage is 25mV \sim 50 mV \sim 75 mV \sim 100 mV, respectively



Figure 3.2(b) Drive level charge density versus depletion width in the solar cell depicted in Figure 3.2(a)



Figure 3.3(a) Capacitance vs. dc bias for a-SiC window layer of solar cell. The measuring frequency is 100Hz and the temperature is 300K. The amplitude of the alternating voltage is $25\text{mV} \cdot 50 \text{ mV} \cdot 75 \text{ mV} \cdot 100 \text{ mV}$, respectively



Figure 3.3(b) Drive level charge density versus depletion width in the solar cell depicted in Figure 3.3(a)



Figure 3.4(a) Capacitance vs. dc bias for a-SiO window layer of solar cell. The measuring frequency is 100Hz and the temperature is 300K. The amplitude of the alternating voltage is $25\text{mV} \cdot 50 \text{ mV} \cdot 75 \text{ mV} \cdot 100 \text{ mV}$, respectively



Figure 3.4(b) Drive level charge density versus depletion width in the solar cell depicted in Figure 3.4(a)



Figure 3.5 Drive level charge density as a function of depletion width of two different



Figure 3.6 Drive level charge density as a function of depletion width of two different types of a-Si solar cells (see text)



Figure 3.7 Illuminated J-V parameters of a-Si p-i-n solar cells by temperature measurement a-Si p-i-n solar cells for deposited p layers (a)µc-Si, (b) a-SiC, (c)a-SiO



Figure 3.8 The normalized initial open circuit voltage as a function of temperature of three different types of a-Si solar cells (see text)



Figure 3.9 The normalized initial short circuit current as a function of temperature of three different types of a-Si solar cells (see text)



Figure 3.10 The normalized initial conversion efficiency as a function of temperature of three different types of a-Si solar cells (see text)



Figure 3.11 Forward bias J-V characteristics for a-Si solar cells with different temperature



5 illumination conditions



Figure 4.2 Quantum efficiency spectra for µc-Si solar cells prepared at different i-layer deposition pressures



Figure 4.3 Band diagram of p-i-n junction by oxygen diffuse grain boundary process



Figure 4.4 Dark and photo conductivity at room temperature for μ c-Si solar cells prepared at different i-layer deposition pressures



Figure 4.5 Dark conductivity at room temperature and activation energy measured at 300K-370K for μ c-Si solar cells prepared at different i-layer deposition pressures



Figure 4.6(a) Capacitance versus dc bias for μ c-Si solar cells at i-layer deposition pressure: 4Torr. The measuring frequency is 100Hz and the temperature is 300K.The amplitude of the alternating voltage is 25mV \cdot 50 mV \cdot 75 mV \cdot 100 mV, respectively



Figure 4.6(b) Drive level charge density versus depletion width in the solar cell depicted in Figure 4.6(a)



Figure 4.7(a) Capacitance versus dc bias for μ c-Si solar cells at i-layer deposition pressure : 6Torr. The measuring frequency is 100Hz and the temperature is 300K. The amplitude of the alternating voltage is 25mV \cdot 50 mV \cdot 75 mV \cdot 100 mV, respectively



Figure 4.7(b) Drive level charge density versus depletion width in the solar cell depicted in Figure 4.7(a)



Figure 4.8(a) Capacitance versus dc bias for μ c-Si solar cells at i-layer deposition pressures : 8Torr. The measuring frequency is 100Hz and the temperature is 300K. The amplitude of the alternating voltage is $25mV \cdot 50 mV \cdot 75 mV \cdot 100 mV$, respectively



Figure 4.8(b) Drive level charge density versus depletion width in the solar cell depicted in Figure 4.8(a)



Figure 4.9 Drive level charge density as a function of depletion width of for μ c-Si solar cells prepared at different i-layer deposition pressures (see text)



Figure 4.10(a) Forward bias J-V characteristics for μ c-Si solar cells prepare at i layer deposition pressure (4Torr) with different temperature



Figure 4.10(b) Forward bias J-V characteristics for μ c-Si solar cells prepare at i layer deposition pressure (6Torr) with different temperature



Figure 4.10(c) Forward bias J-V characteristics for μ c-Si solar cells prepare at i layer deposition pressure (8Torr) with different temperature



Figure 4.11 Illuminated J-V parameters of μ c-Si p-i-n solar cells by temperature measurement for i layers deposited at deposition pressure (a) 4Torr, (b) 6Torr, (c) 8Torr



Figure 4.13 The normalized initial short circuit current as a function of temperature of μ c-Si solar cells prepared at different i-layer deposition pressures (see text)



Figure 4.14 The normalized initial conversion efficiency as a function of temperature of μ c-Si solar cells prepared at different i-layer deposition pressures (see text)

Table

Table 3.1 Illuminated J-V parameters of a-Si p-i-n solar cells for deposited different p layers

Sample	P-layer	Voc (V)	Jsc (mA/cm ²)	FF	Efficiency (%)
Α	µc-Si	0.71	12.0	0.57	4.79
В	a-SiC	0.78	11.3	0.63	5.43
С	a-SiO	0.81	11.5	0.65	5.75



Table 3.2 Parameters of change of a-Si p-i-n solar cells for deposited different p layers

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by temperature effect

P-layer	ΔVoc	ΔJsc	ΔEfficiency
μc-Si	-4.63%	2.94%	1.13%
a-SiC	-3.55%	1.17%	3.41%
a-SiO	-1.96%	0.7%	14.8%

				-	, 1 J	
	P layer : μc-Si		P layer : µc-Si		P layer : µc-Si	
	n	J ₀	n	\mathbf{J}_{0}	n	J ₀
25°C	8.1	2.1E-04	3.5	7.4E-06	18.2	2.1E-02
65℃	8.4	6.2E-04	3.5	1.9E-05	1612	2.4E-02
85℃	7.7	1.6E-03	3.6	1.2E-04	15.4	3.0E-02

Table 3.3 Temperatures correspond to the value of n and J_0 of a-Si p-i-n solar cells for deposited μ c-Si p layers at V=0.1V~0.5V, V=0.7V~0.8V, V=1.2~1.3V, respectively



Table 4-1 Illuminated J-V parameters of µc-Si p-i-n solar cells for i layers deposited at different deposition pressure

Sample	Pressure (Torr)	Voc (V)	Jsc (mA/cm ²)	FF	Efficiency (%)	Rs (Ω)	Rsh (Ω)
Α	4.0	0.48	9.71	0.51	2.34	7.45	223.78
В	6.0	0.42	14.6	0.61	3.73	3.88	549.04
С	8.0	0.45	17.9	0.62	5.05	3.46	1447.97

sample	Pressure (Torr)	Dark conductivity	Photo conductivity	Crystalline volume	SC	Ea (meV)	$\sigma_{ heta}$
				fraction			
А	4.0	2.2E-07	1.0E-04	62.5	1.96	478	20.70
В	6.0	3.8E-08	5.5E-05	69.0	1.38	534	97.71
С	8.0	2.2E-08	2.9E-05	59.0	1.19	539	12.62

Table4-2 The parameters of µc-Si p-i-n solar cells for i layers deposited at different deposition pressure

ATTIMINA. Table4-3 Temperatures correspond to the value of n and J_0 of μ c-Si p-i-n solar cells for i layers deposited at different deposition pressure and (a) at V= $0.2V \sim 0.4V$ (b)at TITIT V=0.6V~1V Mun un

(a)

	4Torr		6Torr		8Torr	
	n	J ₀	n J ₀		n	J ₀
25°C	2.1	4.5E-07	2.0	1.4E-06	2.2	2.0E-06
45°C	2.3	9.8E-07	2.0	2.0E-06	2.2	2.6E-06
65°C	2.3	1.5E-06	2.4	3.5E-06	2.2	4.6E-06
85°C	2.4	3.0E-06	2.4	5.4E-06	2.1	6.5E-06

(b)						
	4Torr		6Torr		8Torr	
	n	\mathbf{J}_{0}	n	\mathbf{J}_{0}	n	\mathbf{J}_{0}
25°C	6.7	2.8E-04	7.4	5.7E-04	7.7	3.4E-04
45°C	7.7	1.8E-04	7.1	6.2E-04	7.1	4.1E-04
65°C	8.1	2.2E-04	7.1	6.4E-04	7.0	3.7E-04
85℃	8.3	2.1E-04	6.8	8.5E-04	6.9	6.3E-04

Table4-4: Parameters of change of µc-Si p-i-n solar cells for i layers deposited at different deposition pressure by temperature effect

Pressure	ΔVoc	s μ ΔJsc	ΔEfficiency
4Torr	-11.5%	0.36%	-12.5%
6 Torr	-8.38%	0.84%	-10.6%
8 Torr	-6.44%	0.9%	-7.56%