Development of new materials for solar cells in Nagoya Institute of Technology

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Abstract

Solar cells with high efficiency and low price have long been desired, however, the commercially available solar cells are still expensive and the efficiencies of them are not high enough yet. A tandem solar cell was fabricated to develop a high-efficiency solar cell, and amorphous carbon solar cells were fabricated to develop a low-price solar cell.

An AlGaAs/Si tandem solar cell was successfully fabricated by heteroepitaxial growth of AlGaAs on Si substrate. At first, a p–n junction was formed in Si substrate by the impurity diffusion method. Then, an AlGaAs p–n junction was grown by MOCVD. Since the AlGaAs p–n junction has a graded band gap emitter, the photo-excited minority carriers can be collected efficiently. The energy conversion efficiency of AlGaAs/Si tandem solar cell was 21.4% (AM0) in spite of large lattice mismatch and difference in thermal expansion coefficients between AlGaAs and Si.

Solar cells were fabricated by using amorphous carbon films deposited by Ion Beam Sputtering and Pulse Laser Deposition (PLD). The highest efficiency of 1.82% (AM0) was attained with a-C(IBS)/p-C(pyrolysis)/p-Si structure. Solar cells using a-C:H were also fabricated by PLD and Plasma CVD, and the efficiencies of them were 2.1% (AM1.5) and 0.04% (AM0), respectively.

Other research activities on solar cells in Nagoya Institute of Technology are briefly mentioned.

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Keywords: Solar cell; AlGaAs/Si; Heteroepitaxy; Amorphous carbon

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1. Introduction

Photovoltaic (PV) system has been expected to supply renewable energy in the near future. Although many efforts have been made on the developments of low-price solar cells with high efficiency, the efficiency of solar cell is still low and the price is high. In this paper, several experimental works to achieve new solar cells with higher efficiency and lower price, which have been conducted in Nagoya Institute of Technology are reviewed.

2. High-efficiency solar cells by material integration

The efficiency of solar cell is low because the energy densities of solar light are low both per wavelength and per area. A properly designed semiconductor p–n junction can convert the incident photon energy to electric power with almost 100% efficiency, if the photon energy is same as the band gap of the semiconductor. However, even if the incident photon energy increased, it generates the same electric power and the conversion efficiency decreases. If the incident photon energy is lower than the band gap of the semiconductor, it cannot generate any electric power, and the efficiency becomes zero. As the spectrum of the solar radiation is fairly broad from UV to IR, only 20% and a little more of solar energy is converted to electric power by the semiconductor p–n junction.

A tandem solar cell which has two semiconductor p–n junctions with different band gap can generate more electric power than a simple solar cell, because it generates electric power using both shorter and longer wavelength light, at the top wide gap and bottom narrow gap semiconductor, respectively. This type of solar cell is expected to achieve the conversion efficiency higher than 30%.

In general, both the operating voltage $V$ and the operating current $I$ are lower than the open circuit voltage $V_{oc}$ and the short circuit current $I_{sc}$, respectively. The ratio of $V/I$/$V_{oc}$/$I_{sc}$ is called fill factor (FF) and, in general, it increases with the input light intensity. Therefore, if the solar radiation is concentrated by the use of an optical lens, the efficiency ($\eta$) of the solar cell increases. It also implies that if we use a multi-junction tandem cell without a light concentrator, the FF will decrease and the total efficiency will not increase. When a triple-junction cell is fabricated properly, the conversion efficiency will be expected to exceed 40%. However, farther increase in the conversion efficiency is fairly difficult even if a solar cell with more junctions is prepared. The key technology for multi-junction solar cell is to prepare a composite material with wide gap and narrow gap semiconductors.

3. GaAs and related materials on Si substrate

3.1. Heteroepitaxial growth of GaAs on Si substrate and AlGaAs/Si tandem solar cell

An AlGaAs solar cell was grown on (100) Si substrate which is oriented 2° off toward [011], by a RF heated metal-organic chemical vapor deposition (MOCVD) at atmospheric pressure. Before this heteroepitaxial growth, a p–n junction and a back surface field (BSF) layer were formed by thermal diffusion of B and P in the Si substrate. AlGaAs layers were grown with trimethylgallium (TMG), trimethylaluminium (TMA) and arsine (AsH₃). Diethyli zinc (DEZ) and hydrogen selenide (H₂Se) were used as p- and n-type dopants, respectively. The two-step growth method and in situ thermal cycle annealing (TCA) were adopted. Before the growth of GaAs, Si substrates were heated at 1000 °C for 5 min to clean up the surface. The off angle Si wafer and a high temperature annealing before crystal growth are important to prevent a formation of anti-phase domain (APD) in GaAs layer. The TCA was performed during AlGaAs buffer layer growth by changing temperature from 300 to 1000 °C and it is effective to reduce the dislocation density generated by the lattice mismatch between the grown crystal and the substrate. The substrate temperature of the main growth process was 800 °C. The temperature sequence is shown in Fig. 1.

The typical structure [1] of Al₀.₁₅Ga₀.₈₅As/Si monolithic tandem solar cell is shown in Fig. 2. The thicknesses of p⁺ graded band gap emitter layer (GBEL), n base layer and n⁺ buffer layer are 0.3, 1.0 and 2.5 µm, respectively. Al content of GBEL varies from 0.15 to 0.30. Buffer layer thickness was 2.5 µm. Al₀.₈Ga₀.₂As is used as window layer with a thickness of 50 nm. The $J$–$V$ characteristics under AM0 one sun illumination and the photovoltaic characteristics of
the cell are shown in Fig. 3 and Table 1, respectively. From the experimental data of short circuit current density for the top cell and for the bottom cell, coincident to each other at the value of 23.8 mA/cm$^2$, it is evident that exact current matching between the two cells are achieved. Under AM0 and 1 sun conditions at 27 °C, the active area conversion efficiency of 21.2% was achieved with a two-terminal configuration and 21.4% with a four-terminal configuration.

A GaAs solar cell grown on Si substrate has higher radiation tolerance than that on GaAs. For example, the reverse bias dark saturation current of GaAs solar cell on GaAs substrate increased by approximately three orders of magnitude after $10^{16}$ cm$^{-2}$ irradiation of 1 MeV electrons, but the same treatment caused only a little change to the GaAs solar cell on Si substrate [2]. The saturation current of the GaAs/Si cell is larger than that of the GaAs/GaAs cell before irradiation because of the high dislocation density.

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3.2. Passivation of electrical active defects in GaAs by hydrogen plasma

Although the dislocation density in GaAs layer at the crystal growth temperature can be reduced to $10^4$ cm$^{-2}$ by a few cycles of TCA, the difference in thermal expansion coefficients between GaAs and Si induces very high stress in GaAs layer during the cooling process down to room temperature, and a lot of dislocations are introduced to relieve the stress [3]. More than $10^6$ cm$^{-2}$ dislocations act as minority carrier traps and decline the solar cell performance.

Hydrogen atoms can terminate the dangling bond at the crystal defect and make the defect level electrically inactive. Several experiments have been done to passivate the recombination centers with $H_2$ [4] and PH$_3$ plasma [5]. The hydrogen plasma was generated by RF power in a low pressure MOCVD reactor, and a GaAs/Si sample was placed at the downstream area as shown in Fig. 4. After the hydrogen plasma treatment for 2 h, the carrier concentration in GaAs layer decreased and a broad deep level emission appeared in the photoluminescence (PL) spectrum. After successive annealing at 450 °C for 10 min in AsH$_3$/H$_2$ atmosphere, the carrier concentration recovered the initial
value, the deep level PL emission disappeared, and the free exciton peak in PL spectrum increased.

A GaAs solar cell was grown on Si substrate and the effect of the plasma exposure was studied [6]. The crystal growth method is almost the same as mentioned above. After the growth process, the passivation was carried out in PH$_3$/H$_2$ (PH$_3$/H$_2$ = 0.1, in ccm) atmosphere. The plasma is excited by RF power (13.56 MHz) with a copper coil encircling the gas entrance of the quartz chamber. The pressure, RF power, sample temperature and plasma exposure time were 13 Pa, 90 W, 250 °C and 1 h, respectively. After the plasma exposure, top and bottom electrodes and MgF$_2$/ZnS antireflection films were formed. Fig. 5 shows the photovoltaic $I$–$V$ characteristics of GaAs solar cells grown on Si substrates before and after PH$_3$/H$_2$ plasma exposure. The result in the case of pure H$_2$ plasma is also shown. Compared with the untreated cell, the H$_2$ plasma-passivated cell shows increases in both the $J_{sc}$ and $V_{oc}$, from 34.08 to 34.46 mA/cm$^2$, and from 0.85 to 0.88 V, respectively. The saturation current density $J_0$ of H$_2$ plasma-exposed cell shows a slight decrease from $1.14 \times 10^{-9}$ to $7.84 \times 10^{-10}$ A/cm$^2$ compared to that of the as-grown cell. For PH$_3$ + H$_2$ plasma-passivated cell, the lowest value of $J_0$ $5.72 \times 10^{-11}$ A/cm$^2$, was obtained. As a result, the conversion efficiency ($\eta$) increased from 15.9 to 17.6%. In the case of the PH$_3$ + H$_2$ plasma-passivated cell, higher $V_{oc}$ (0.93 V) was obtained due to the very low value of $J_0$, leading to further improvement in $\eta$ (18.6%). The photovoltaic characteristics of the plasma-passivated cells are summarized in Table 2.

### 4. Amorphous carbon for low price and environment-friendly solar cells

Silicon is classified into group IV in the periodic table and amorphous Si (a-Si) is a popular material for solar cells. Carbon is also one of the group IV elements and amorphous C (a-C) is expected to behave like a-Si if it is properly prepared. The atomic bond between two Si atoms is sp$^3$ bond and Si crystallizes into diamond structure. On the other hand, the sp$^2$ bond is more likely realized between two C atoms which usually form graphite, or sometimes fullerenes, nano-tubes and so on. Only in the case of diamond crystal, the sp$^3$ bonds are realized among C atoms. The band gap $E_g$ of a-C depends on the sp$^2$/sp$^3$ ratio, and it can be tailored by the control of the preparation conditions. If high quality a-C films with different band gaps can be prepared, a tandem solar cell of environment-friendly material will be realized.

#### 4.1. Amorphous carbon film prepared from camphor

Since camphor (C$_{10}$H$_{16}$O) has both sp$^2$ and sp$^3$ hybridized bonds as shown in Fig. 6, it was used as starting material to prepare a-C films with various sp$^2$/sp$^3$ ratios.

Pyrolysis (thermal CVD) of carbon films was carried out using a double furnace setup, one furnace was used for heating the source material (camphor) at a temperature range from 110 to 140 °C, and the other for controlling the substrate temperature at 650 °C, using Ar as carrier gas. The deposition was done for about 2 h, resulting in a p-type film of 20–25 nm thick [7].

Ion Beam Sputtering (IBS) [8] and Pulsed Laser Deposition (PLD) were also used to prepare carbon films. In these cases, camphor was burnt in a quartz tube 1-m long and 11-cm diameter. A schematic diagram of the experimental setup constructed for the formation of carbon soot is shown in Fig. 7. The soot deposited along the tube walls was collected, dried in the oven for an hour and pressed into

| $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%) | $\eta$ (%) |
|-------------|---------------------|--------|-----------|
| As-grown    | 0.85                | 34.08  | 73.9      | 15.9      |
| H$_2$       | 0.88                | 34.46  | 78.6      | 17.7      |
| PH$_3$ + H$_2$ | 0.93            | 33.39  | 80.9      | 18.6      |
pellets. These pellets were used as targets to prepare carbonaceous thin films by IBS or PLD. Undoped C film prepared by IBS was n-type.

Amorphous carbon films were deposited on Si substrates by excimer laser (XeCl, $\lambda = 308$ nm, $\tau = 20$ ns, repetition rate $= 2$–5 Hz, spot size $= 5.5$ mm$^2$), which is focused on the target at an incident angle of $45^\circ$ to the target normal. The substrate was mounted parallel to the target surface at a distance of 45 mm. The laser pulse energy was 150 mJ on the window. In order to dope, the camphoric carbon (CC) soot was mixed with various amount of red phosphorus [9] or boron [10] and compressed into pellets.

Heterojunctions of P-dope C on n-Si and B-dope C on p-Si showed ohmic $I$–$V$ characteristics and P-dope C on p-Si and B-dope C on n-Si showed rectifying $I$–$V$ characteristics and photovoltaic effect. The energy conversion efficiencies of P-dope C/p-Si and B-dope C/n-Si solar cells were 1.25 and 0.2%, respectively. The best performance as a solar cell was obtained with n-C/p-C/p-Si structure [11]. In this cell, the top 100 nm n-C and bottom 60–70 nm p-C layers were deposited on p-Si substrate by IBS and pyrolysis, respectively. The photovoltaic characteristics of this cell is shown in Fig. 8. $V_{oc}$, $I_{sc}$, FF and $\eta$ were 0.339 V, 17.1 mA/cm$^2$, 42.3 and 1.82%, respectively.

It is well known that the addition of H atoms to an a-Si film improves its electrical properties. In order to add some H atoms to a-C prepared by PLD, the mixture of graphite and camphor (1 wt%) was used as a target. In this experiment, camphor was not burnt to maintain a certain amount of H atoms within the target. Using the same PLD setup, and adjusting the laser pulse to 130 mJ and 6 Hz, a-C:H films were deposited on p-Si wafer, and characterized as a solar cell under AM1.5 and 1 sun conditions.
the structure of Au (12–15 nm)/a-C:H (120 nm)/p-Si wafer/Au (100 nm), $V_{oc}$, $I_{sc}$, FF and $\eta$ were 0.4 V, 15 mA/cm$^2$, 38 and 2.1%, respectively [12]. The $I-V$ characteristics of the cell in dark and illuminated conditions are shown in Fig. 9.

4.2. Amorphous carbon films prepared from methane

 Plasma CVD using SiH$_4$/H$_2$ gas gives high quality a-Si:H film and high performance solar cells. If the formation of sp$^2$ bonds can be controlled, the plasma CVD using CH$_4$/H$_2$ will give high quality a-C:H films. This process is expected to provide large area solar cells with very low cost.

 A plasma CVD reactor, using a capacitively coupled parallel-plate, operating at 13.56 MHz was used to deposit a-C:H films on Si substrate which was kept at 300 K by water cooling sample holder. No bias voltage was intentionally applied between the substrate holder and the chamber wall, and a low self-bias was induced between the plasma and the substrate. H$_2$, CH$_4$ and 1% trimethylboron (TMB) in H$_2$ were used as the sources and the flow rates were maintained at 300, 10 and 40 sccm, respectively. The RF power was 300 W (0.87 W/cm$^3$) and the duration of deposition was 1 h. The chamber pressure was controlled to keep the CH$_4$ partial pressure as $P_{CH4}=6$ Pa [13].

 The heterojunction solar cell of B-doped a-C(H)/n-Si was characterized under AM1.5 and 1 sun conditions. $V_{oc}$, $I_{sc}$, FF and $\eta$ were 0.22 V, 0.35 mA/cm$^2$, 48 and 0.04%, respectively.

5. Other activities

 In a GaAs/Si tandem solar cell, more solar photons will be absorbed in the GaAs cell than in the Si cell because the band gap of GaAs is not wide enough, and the current matching between the top and the bottom cells cannot be achieved. Although an Al$_{0.22}$Ga$_{0.78}$As layer will absorb the same number of photons as the Si substrate do, they will not produce the same current. In general, the dislocation density in AlGaAs grown on Si substrate increases with the Al content, and the quantum efficiency of AlGaAs solar cell on Si decreases. Many efforts [14–19] have been done to improve the crystal quality of GaAs and AlGaAs on GaAs, for many years. InGaP is also being investigated [20] as a material for top cell instead of AlGaAs. As an alternative method to fabricate a tandem solar cell, the bonding of GaAs wafer to Si wafer is also under investigation [21–23].

 In order to prepare low cost solar cells, polycrystalline GaAs on glass substrate has been attempted [24]. TiO$_2$ solar cells are also studied [25]. Though the TiO$_2$ cell is expected to have relatively high efficiency and to be fabricated with low cost, a wet cell is not convenient to manipulate. In order to develop a dry TiO$_2$ cell, PLD deposited CuI was studied as a solid state electrolyte [26]. The addition of H atoms to a-C by plasma CVD was not effective to terminate the dangling bonds in a-C, and seemed to convert the a-C film into organic polymeric materials. Therefore, solar cells using organic polymer are also under investigations [27].

6. Conclusions

 The research activities on solar cell materials in Nagoya Institute of Technology were reviewed.

 Although the III–V materials on Si substrate are the candidates for high-efficiency solar cells, how to integrate the materials with different physical properties is the key technology and one more breakthrough is required to achieve the final target.

 Amorphous carbon was expected to behave like an amorphous silicon, but it was not true. The band gap of a-C could be adjusted for solar cell application by controlling the deposition conditions. However, the conductivity control of it is difficult. Addition of hydrogen to a-C film is not effective to terminate the dangling bond. Carbon films containing much hydrogen atoms seem to be gradually changed to a polymer like material. In this sense, a solar cell based on organic polymer is expected to be a next generation solar cell.

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