Hydrogenated Amorphous Silicon Thin Films as Passivation Layers Deposited by Microwave Remote-PECVD for Heterojunction Solar Cells

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An intrinsic silicon thin film passivation layer is deposited by the microwave remote-plasma enhanced chemical vapor deposition at temperature of 175 °C and various gas ratios for solar cell applications. The good quality amorphous silicon films were formed at silane (SiH_4) gas flow rates above 15 sccm. The highest effective carrier lifetime was obtained at the SiH_4 flow rate of 20 sccm and the value was about 3 times higher compared with the bulk lifetime of 5.6 μs at a fixed injection level of $\Delta n = 5\times10^{14}$ cm^{-3}. An annealing treatment was performed and the carrier life times were increased approximately 5 times compared with the bulk lifetime. The optimal annealing temperature and time were obtained at 250 °C and 60 sec respectively. This indicates that the combination of the deposition of an amorphous thin film at a low temperature and the annealing treatment contributes to the excellent surface and bulk passivation.

Keywords: Microwave, Solar cells, Thin film, Heterojunction, Passivation layer

1. INTRODUCTION

Single crystalline silicon (sc-Si) and multicrystalline silicon (mc-Si) solar cells are mainly fabricated by thermal diffusion process at a high temperature above 800 °C. In contrast, thin film silicon solar cells using hydrogenated amorphous silicon (a-Si:H) film and hydrogenated microcrystalline silicon (μc-Si:H) film do not need a high temperature. Heterojunction structures using impurity doped a-Si:H or μc-Si:H have been attempted to realize high-efficiency n^+ a-Si:H or n^+ μc-Si:H/p c-Si solar cells [1,2]. However, this has not been practical due to the reason that the recombination velocity of carrier (S_r) at a-Si:H/c-Si interface was high. Recently, for the reduction of S_r and obtaining a high performance solar cell, a new concept structure inserting a-Si:H film as intrinsic layer between emitter thin film and base c-Si called a HIT™ solar cell has been proposed by the Sanyo group[3]. These films are usually deposited by a direct plasma-enhanced chemical vapor deposition (PECVD) technique. However, it may have inherent drawbacks such as damage on growing film caused by high energy particles. For these reason, many studies have been demonstrated in avoiding the damage of plasma[4-7]. Among these, a remote-PECVD has some advantages in the deposition at low temperatures and a high deposition rate because of the high plasma density and less ion bombardment on the surface[8]. This study reports on developing the microwave remote-PECVD (MW remote-PECVD) method to deposit intrinsic silicon films, applicable to solar cells. The deposition process with the variations of the gas ratio r_H (=H_2/SiH_4) was investigated. The structural properties and effective carrier lifetime (τ_{eff}) of the intrinsic silicon films deposited at various deposition conditions are reported. In addition, the thermal annealing treatment after the deposition of the intrinsic silicon films on c-Si wafer is carried out and the characteristics are examined.

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2. EXPERIMENT

MW remote-PECVD was used to deposit intrinsic silicon thin films[9,10]. The schematic of the deposition reactor used in this experiment is shown in Fig. 1. The hydrogen (H_2) gas was introduced into the chamber through a trumpet-like quartz tube with a 1/2-inch diameter, and it was discharged by employing a 2.45-GHz microwave to generate high-density hydrogen radicals. For the deposition of a-Si:H thin films, silane (SiH_4) gas was introduced as the Si source from a ring-type tube having many orifices and the generated hydrogen radicals reacted with SiH_4 molecules. When one SiH_4 molecule is decomposed by hydrogen radicals, it produces five radicals, one Si and four H atoms.

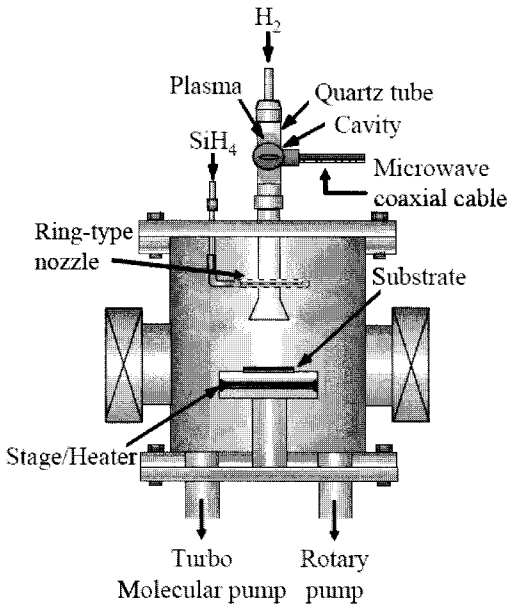

Fig. 1. Schematic of microwave remote-plasma enhanced chemical vapor deposition (MW remote-PECVD) apparatus.

Table 1. Deposition conditions for the intrinsic silicon thin films as a passivation layer prepared by MW remote-PECVD.

H_2 [sccm]	SiH_4 [sccm]	Power [W]	Temp. [°C]	Press. [Torr]	Gas ratio r_H
80	5	50	175	0.5	16
80	10	50	175	0.5	8
80	15	50	175	0.5	5.3
80	20	50	175	0.5	4

These are the primary radicals available for the film deposition process. The change of deposition conditions is expected to change the proportion of atomic Si and atomic H in the gas phase. Since Si and H are highly reactive with SiH_4, they react with ambient SiH_4, forming hydrogen rich species such as SiH_3 and SiH_2, which further contribute to the film deposition.

The distance between the center of microwave cavity and the substrate was approximately 145 mm. The lower end of the quartz tube and ring-type nozzle from the substrate was positioned at 30 mm and 55 mm, respectively. In order to investigate the properties of as-deposited silicon thin films as the passivation layer at varied deposition conditions, p-type Cz (100) silicon substrate was used. The wafer was cut into 2 cm×2 cm substrates, etched in HF:6HNO_3 solution to remove saw damage, dipped in 5 % HF solution to remove the native oxide layer and rinsed in pure water. After that, the substrate was located into the experimental vacuum chamber. The substrate was heated in the vacuum chamber with a pressure of 2×10^{-5} Torr. Then, the SiH_4 and H_2 gas was introduced for the deposition of silicon thin film. The H_2 gas flow rate was fixed to 80 sccm, and the SiH_4 flow rates were changed, i.e., various deposition gas ratios r_H (= H_2/SiH_4).

All the control time for introducing experimental gas conditions was performed within 1 min. For deposition, the temperature and working pressure were fixed to 175 °C and 0.5 Torr, respectively. The detailed deposition parameters were shown in Table 1. The thicknesses of silicon thin films deposited on glass substrates (Corning #1737) were measured by a DEKTAK thickness profilometer. Fourier Transform Infrared Spectrometer (FT-IR) measurement was used to evaluate the film contents including the hydrogen bonds. In addition, to the examination of the effective carrier lifetimes of the wafers, the Quasi Steady State Photo conductance (QSS-PC) was used[11].

3. RESULTS AND DISCUSSION

3.1 Variation of silicon thin films deposited at different gas ratios

The films were deposited on a glass substrate for 60 min at temperature of 175 °C in order to investigate the film properties deposited at varied gas ratios r_H. The structural properties and thickness were measured by X-ray diffraction (XRD) measurement and thickness profilometer, respectively. Figure 2 shows the (a) XRD patterns and (b) deposition rates of as-deposited samples at varied gas ratios. As shown in Fig. 2(a), the peaks of silicon crystalline orientation (111), (220) and (311) at a silane flow rate of 5 sccm were detected.

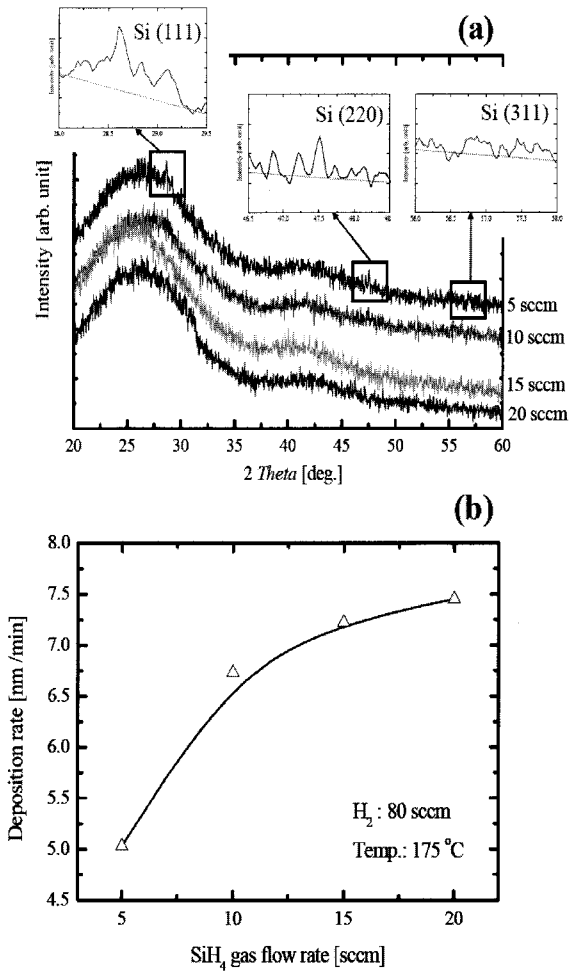

Fig. 2. (a) XRD patterns and (b) deposition rates as a function of silane (SiH_4) flow rates.

The peaks of crystalline orientation (220) and (311) at a silane flow rate of 10 sccm were also slightly revealed and shows that the films were crystallized with decreasing SiH_4 gas flow rates at a relatively low temperature of 175 °C. When the SiH_4 gas flow rates were increased, i.e., decrease in gas ratios r_H, the silicon peaks did not appear and indicates that the films are hydrogenated amorphous silicon (a-Si:H). For measuring the thicknesses of as-deposited films on glass substrates at varied r_H, half of the samples were etched in a diluted potassium hydroxide (KOH) solution. The step height between the as-deposited films and the etched layer on the glass substrate was determined and the deposition rates were calculated. The deposition rate of as-deposited film increased with an increasing SiH_4 gas flow rate as shown in Fig. 2(b). The thicknesses increased from approximately 300 nm to 500 nm. It is due to the increase in total gas flow rate and decomposition rate of SiH_4 gas by the generated hydrogen radicals.

To apply the films as a passivation layer for solar cells, the films were deposited on Cz (100) single crystalline silicon (c-Si) substrate at varied SiH_4 gas rates that ranged from 5 to 20 sccm. The deposition temperature and introduced hydrogen (H_2) gas flow rate were set to 175 °C and 80 sccm, respectively. The film thicknesses were fixed

to 20 nm. For evaluating the bonding structures of the as-deposited films on Cz c-Si substrates, the samples were measured by FT-IR measurement. Figure 3 shows the FT-IR absorption spectra, which were converted from the measured transmittance using the Beer-Lambert law, and the hydrogen content (C_H), which was estimated from the FT-IR absorption spectra[12]. As shown in Fig. 3(a), two dominant peaks were revealed at wavenumber 2000 cm^{-1} and 2090 cm^{-1}. The wavenumber 2000 cm^{-1} peak means the stretching mode of the Si-H bond and the wavenumber 2090 cm^{-1} peak shows the stretching mode of the Si-H_2 bond, respectively. The bond changes occurred with increasing SiH_4 flow rates. The Si-H stretching mode was mainly formed at high SiH_4 flow rates above 15 sccm, and the Si-H_2 stretching mode (which means defects in the film) was formed mainly at low SiH_4 flow rates below 10 sccm. The appearance of Si-H_2 stretching mode might be the increase of a dangling bond in the film due to the micro-crystallization of film as shown in Fig. 2(a). The intensity of the Si-H stretching mode was increased by increasing the SiH_4 flow rates. It indicates that good quality a-Si:H thin films are formed due to the increase in the decomposition rate of SiH_4 gas in these experimental conditions. From these results, we can assume that the high quality a-Si:H thin films are obtained at high SiH_4 flow rates above 15 sccm, i.e., low gas ratios r_H below 5.3.

To investigate the quality of films deposited at varied SiH_4 flow rates, the C_H was evaluated from the C_H was evaluated from the FT-IR absorption spectra as shown in Fig. 3(a). The C_H was calculated from the following ratio:

$$C_H = [N_H/(N_H + N_{Si})] \times 100\ [at.\%].$$

Where, the N_{Si} and N_H are the density of the silicon atoms (N_{Si}=5×10^{22} cm^{-3}) and the density of the Si-H_n bond, respectively. The density of the Si-H_n bond N_H can be calculated using the relationship $N_H=A\int[\alpha(\omega)/\omega]d\omega$ integrated on the 2000~2100 cm^{-1} band, in which A is a constant[13,14], and $\alpha(\omega)$ is the absorption coefficient at frequency ω. The variation in the C_H as a function of the SiH_4 flow rate was shown in Fig. 3(b). As seen from the Fig. 3(b), the C_H in the film was increased from 6.6 at.% to 8.5 at.% with increasing SiH_4 flow rates. This implies that the SiH_4 flow rate can control the hydrogen concentration. From the results of FT-IR spectra and C_H, the SiH_4 flow rates above 15 sccm can be considered high quality films, which have a low defect density.

3.2 Effect of annealing treatment

For measuring the effective carrier lifetime (τ_{eff}), boron-doped Cz (100) wafer of about 0.8 Ωcm resistivity and 380 μm thickness were used. The films were bifacially deposited on the prepared wafers at varied gas ratios r_H, i.e., various SiH_4 flow rates. The as-grown wafer surface was chemically passivated with a 3 % iodine/ethanol solution to derive a bulk lifetime. The τ_{eff} of the wafer in symmetric a-Si:H or μc-Si:H/c-Si/a-Si:H or μc-Si:H after deposition of films at varied gas ratios was measured. The values of the carrier lifetimes were obtained at a fixed injection level of Δn = 5×10^{14} cm^{-3} and 1×10^{15} cm^{-3}. Figure 4 shows the

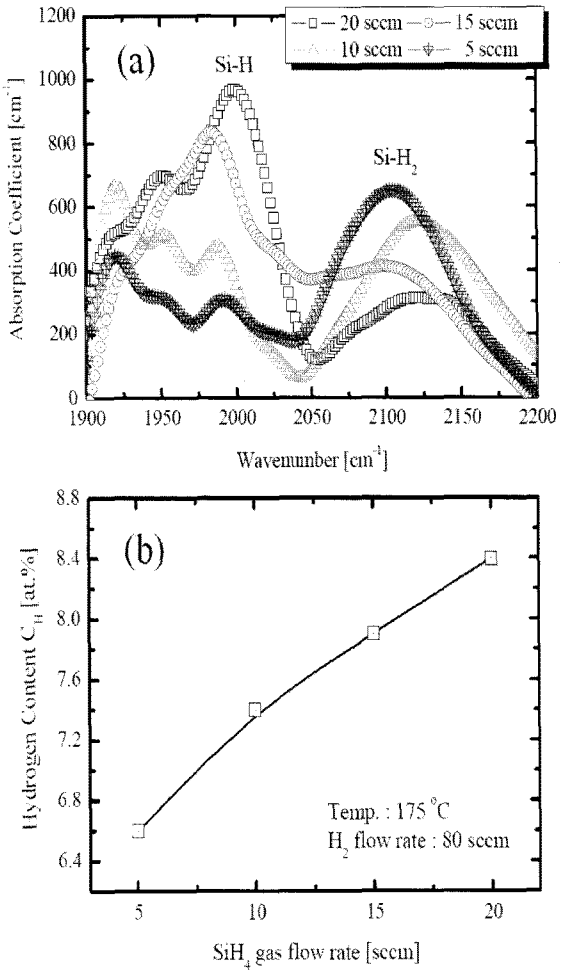

Fig. 3. (a) FT-IR absorption spectra in the wavenumbers range of 1900 ~ 2200 cm^{-1} with variation of SiH_4 flow rates. (b) Hydrogen content (C_H) in films deposited at varied SiH_4 flow rates determined from the FT-IR transmittance spectra.

τ_{eff} versus excess carrier concentration of samples deposited at varied SiH_4 flow rates. The filled black square plots show the chemically passivated (CP) carrier lifetime. The value of carrier lifetime as bulk lifetime was 5.6 μs at a fixed injection level of Δn = 5×10^{14} cm^{-3}.

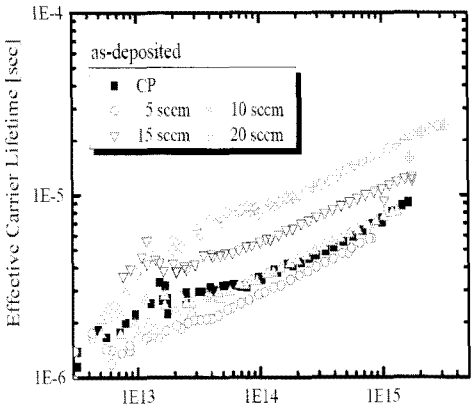

Fig. 4. τ_{eff} versus the excess carrier concentration of the c-Si wafers passivated with bifacial as-deposited films at various SiH_4 flow rates.

When the films were deposited at higher gas ratio above 8, i.e., the SiH_4 flow rates below 10 sccm, the τ_{eff} were 5.3 μs and 6 μs at the SiH_4 flow rate of 5 sccm and 10 sccm, respectively. Its values were near the bulk lifetime. This might be due to the effect of micro-crystallized films, which are deposited at low SiH_4 flow rates below 10 sccm, as shown in Fig. 2(a). It means that the films fabricated at higher gas ratio are low quality including an abundant dangling bond as shown in Fig. 3(a). However, the τ_{eff} was increased with the increasing SiH_4 flow rate. The values were 8.8 μs and 13.3 μs at the SiH_4 flow rate of 15 sccm and 20 sccm, respectively. The highest τ_{eff} was found to have been about 3 times at the SiH_4 flow rate of 20 sccm, which was high compared to the lifetime of the same wafer passivated chemically with 3 % iodine/ethanol solution of approximately 5.6 μs. It indicates that the τ_{eff} depended strongly on the deposition gas ratio r_H. Moreover, the voluminous Si-H bond is corresponds to the τ_{eff} of samples deposited at varied SiH_4 flow rates as shown in Fig. 3(a). It denotes that the Si-H bond (which means a good film quality) was strongly related to the τ_{eff} and passivates the dangling bonds on c-Si surfaces.

For further improvement of carrier lifetime, all the samples deposited at varied r_H were thermally annealed at varied temperatures and annealing duration. To investigate the effect of annealing, all the samples were annealed on a hot plate in air ambient. The dependence of annealing conditions was explored. Figure 5(a) shows the τ_{eff} as a function of annealing duration in as-deposited films at varied SiH_4 flow rates. The annealing temperature was constant at 200 °C, and the annealing duration was increased. As shown in this figure, the τ_{eff} was gradually increased with an increasing annealing duration. In addition, the whole value of τ_{eff} depended on the SiH_4 flow rates. The highest improvement was revealed at the annealing duration of 60 sec and sample with a-Si:H film deposited at SiH_4 flow rates of 20 sccm. The value of τ_{eff} was about 20 μs at a fixed injection level of $\Delta n = 5\times10^{14}$ cm^{-3}. This indicates that the improvement in the effective carrier lifetime was due to the effect of hydrogen content as shown in Fig. 3(b). In particular, when the samples were passivated at SiH_4 flow rates above 10 sccm, the value of τ_{eff} were improved approximately 1.5 ~ 4 times compared with the bulk lifetime.

However, the τ_{eff} of film deposited at SiH_4 flow rate of 5 sccm did not improve with the variation of annealing duration. Assumed is that the effect of high surface recombination velocity between the deposited film, which was micro-crystallized, and c-Si interface due to the low quality film, have $Si-H_2$ and $(Si-H_2)_n$ bonds, as shown in Fig. 3(a). The effect of annealing temperature was subsequently investigated. From the results, the optimal annealing time was selected at 60 sec. Figure 5(b) shows the effect of τ_{eff} on the annealing temperatures of the films deposited at varied SiH_4 flow rates. The τ_{eff} was measured at a 50 °C annealing temperature interval. All the samples deposited at SiH_4 flow rates below 15 sccm were slightly increased with increasing annealing temperature. The τ_{eff} was increased with increasing SiH_4 flow rates. This is due to the hydrogen content as shown in Fig. 3(b). The best τ_{eff} was obtained at the annealing temperature of 250 °C with SiH_4 flow rate of 20 sccm.

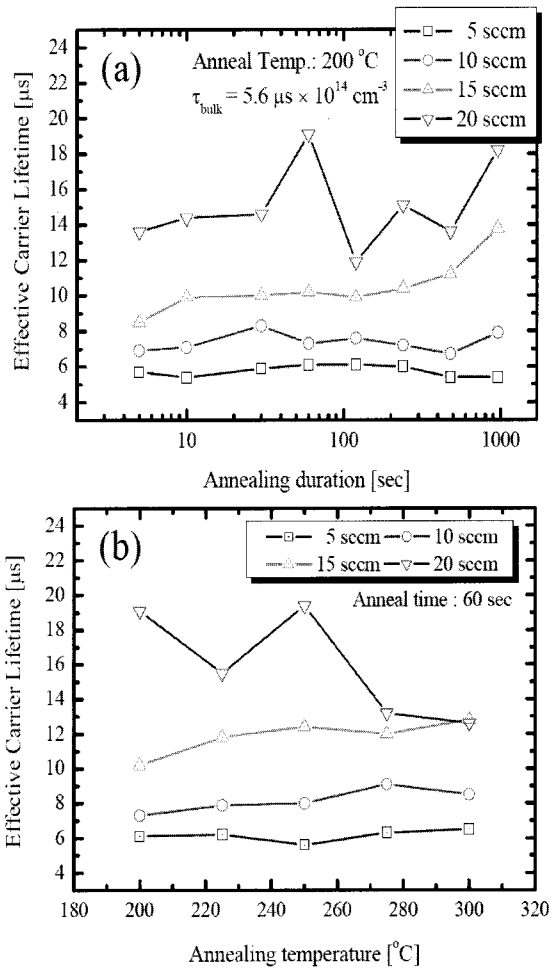

Fig. 5. Dependence of effective carrier lifetime (τ_{eff}) on (a) annealing duration and (b) annealing temperatures in c-Si wafers passivated with bifacial films deposited at varied SiH_4 flow rates. The τ_{eff} was measured by the QSS-PC technique at a fixed injection level of $\Delta n = 5\times10^{14}$ cm^{-3}.

Finally, to investigate the effect of bulk passivation by annealing treatment, the films deposited on the c-Si wafer at varied gas ratios r_H were etched off in an HF: $6HNO_3$ solution and the samples were chemically passivated with a 3 % iodine/ethanol solution to estimate the bulk carrier lifetime. Figure 6 shows the carrier lifetime versus the excess carrier concentration of the samples after annealing treatment. The τ_{eff} in samples of as-deposited films at SiH_4 flow rate above 10 sccm was increased and compared with the lifetime of chemically passivated same wafers as shown in Fig. 4. After the annealing treatment, the carrier lifetimes of all samples were further increased, because the surface of the samples was chemically passivated. In contrast with as-deposited sample, the carrier lifetime of fabricated sample at SiH_4 flow rate of 5 sccm was drastically improved. When the film was deposited at SiH_4 flow rate of 5 sccm, the as-deposited films have a poor passivation layer due to the micro-crystallization on the c-Si surface as shown in Figs. 2(a) and 3(a). However, the silicon dangling bonds in the c-Si region were reduced by thermally activated hydrogen atoms in as-deposited films. When the carrier lifetime was measured after removing the as-deposition layer, the improved carrier lifetime was revealed as shown in Fig. 6.

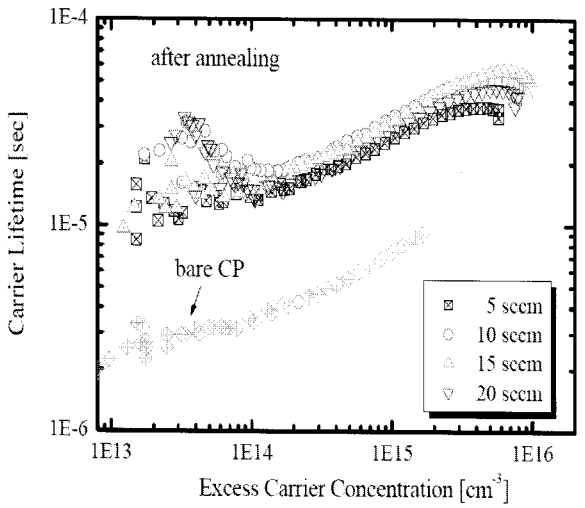

Fig. 6. Carrier lifetime versus the excess carrier concentration of the c-Si wafers passivated chemically with 3 % iodine/ethanol solution after annealing treatment.

The carrier lifetime of all the samples were improved by approximately 5 times compared with the bulk carrier lifetime. The highest value of carrier lifetime after annealing was obtained to 32.5 μs at a fixed injection level of $\Delta n = 1\times10^{15}$ cm^{-3}. Based on the above results, we found that the high quality a-Si:H films could be formed by MW remote-PECVD at relatively low temperature as 175 °C and the increase of the SiH_4 flow rate. Moreover, the annealing treatment is an effective process to improve the bulk property. The τ_{eff} depended strongly on the thin film deposition gas ratios and the annealing treatment. It indicates that the combination of thin film deposition and annealing treatment can improve the τ_{eff} and bulk carrier lifetime due to the strong surface passivation and bulk passivation effect.

4. CONCLUSION

The intrinsic silicon thin film as passivation layer prepared at various deposition conditions was investigated. The good quality amorphous films were formed at SiH_4 gas flow rates above 15 sccm. The highest effective carrier lifetime was obtained at the SiH_4 flow rate of 20 sccm and the value was about 3 times higher compared with the bulk lifetime. The effective carrier lifetime after thermal annealing treatment increased approximately 5 times compared with the bulk lifetime. The optimal annealing temperature and time were realized for obtaining a good passivation effect. The microwave remote-plasma enhanced chemical vapor deposition method is an effective candidate method for application of heterojunction solar cells.

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