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Crystalline silicon surface passivation by intrinsic silicon thin films deposited by low-frequency inductively coupled plasma

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Amorphous and microcrystal hydrogenated intrinsic silicon (a-Si:H/ μ c-Si:H) thin films with good silicon surface passivation effect were deposited using a precursor gases of silane and hydrogen, which were discharged by low frequency inductively coupled high density plasma source. With regard to silicon surface passivation, the effect of discharge power on thin films properties, including the optical band gap, the crystal fraction, and bond configuration, as well as the deposition rate were thoroughly investigated. It was found that the best passivation effect was obtained at the region near the transition regime from a-Si:H to μ c-Si:H with a minimized incubation layer between the passivation layer and substrate. Cz-silicon wafer passivated by as-deposited μ c-Si:H thin films without any post-deposition thermal annealing possesses minority carrier lifetime of about 234 μ s. This is attributed to the chemical annealing from the high-density hydrogen plasma during the deposition process. Subsequent thermal annealing in hydrogen flow increased the lifetime to 524 μ s with a suppressed maximum surface recombination velocity of as low as 60 cm/s. Throughout the process flow covering the pre-deposition H plasma treatment, the film deposition from H₂ diluted feedstock gases and the post-deposition annealing, hydrogen plays a vital role to enhance the minority carrier lifetime by improving the interface properties. The injection level dependent surface recombination velocity was also extracted from the lifetime measurement. The effectivity of the a-Si:H/ μ c-Si:H for silicon surface passivation in a practical heterojunction solar cell was further validated by the excellent photovoltaic performance. © 2012 American Institute of Physics.

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I. INTRODUCTION

Compared with the optical management by conventional methods like an antireflection layer, the minimization of electronic losses at the crystal silicon surface is a more delicate challenge for high efficiency solar.¹ Recombination losses at the silicon interface or surface can be minimized by using two passivation schemes, namely, via chemical passivation or filed passivation. The former aims to reduce the interface defects that originate from the dangling bonds by H atom or a thin dielectric or semiconductor film. The latter is based on the fact that the electron/hole density at the interface will be significantly reduced by formation of a built-in potential from the introduction of a passivation layer. Through these two strategies, various Si-based materials, such as hydrogenated amorphous silicon (a-Si:H),² silicon nitride (SiN),³ thermal oxygenated silicon dioxide (SiO₂),⁴ and amorphous silicon carbide (a-SiC_x)⁵ have been investigated for passivation purposes. Among these materials, a-Si:H is still the best candidate for silicon heterojunction (HT) solar cells^{6,7} due to its excellent passivation properties obtained at low deposition temperatures and also simple processing without the introduction of any atoms other than silicon and hydrogen.

In previous works, the a-Si:H passivation layers were mainly deposited by using conventional capacitively coupled plasma enhanced chemical vapor deposition (PECVD) or hot wire chemical vapor deposition (HWCVD). The only available report on the application of inductively coupled plasma (ICP) in a-Si:H deposition for silicon surface passivation is from Ref. 8, where the ICP source is powered by regular frequency of 13.56 MHz. Using this method, the maximum effective lifetime value of 53 μ s was obtained on *p*-type silicon substrate (resistivity 1–20 Ω cm) with a 15 nm thick a-Si:H passivation layer. In our previous works, we reported the development of low frequency inductively coupled plasma (LFICP) source⁹ and its applications in nanotechnology fabrication^{10,11} and also, the deposition of intrinsic and doped silicon thin films.^{12,13} It was acknowledged that this LFICP source features various inherent advantages such as a high density, axial/radial uniformity plasma, and also independent control of electron number density and the energy of ions impinging on the growing surface. In order to decrease the ion bombardment on semiconductor surface generating more “soft” plasma for high quality interface in solar cell application, this ICP source has been modified into a new version. The distance between the flat RF coil electrode and substrate stage was increased to about 33 cm. Two ring-shaped gas inlets are embedded in the vacuum chamber wall: the top one near the quartz window is used to import

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the diluent gases Ar/H₂, the bottom one located about 10 cm above the substrate stage feeds feedstock gases like SiH₄, PH₃ and B₂H₆, etc., into the reactive chamber. Therefore, as-generated plasma near the substrate stage is like the term of remote plasma.¹⁴

In present work, intrinsic a-Si:H and μ c-Si:H thin films were deposited using the gas mixture of silane and hydrogen discharged by the modified LFICP-source at a low temperature of 140 °C. The discharge power effect on the properties including the optical band gap, crystallinity, and hydrogen content of the thin films were thoroughly investigated with regards to its application in the area of crystal silicon surface passivation. The relationship between the incubation layer thickness and the lifetime values were established. The pre-deposition hydrogen plasma treatment and post-deposition annealing with hydrogen flow were performed to improve the c-silicon/a-Si:H (μ c-Si:H) interface quality, and thus minimize the interface recombination. The high as-deposited lifetime values were obtained and ascribed to the chemical annealing from high-density hydrogen in the process of deposition.

II. EXPERIMENTAL DETAILS

The a-Si:H/ μ c-Si:H thin films of thickness of 50 nm were deposited on the double-side polished, *p*-type Czochralski silicon substrates [resistivity of 8 Ω .cm, thickness of 600 μ m, (100) orientation, and are of about 3 $\times$ 3 cm²]. Prior to being loaded into the vacuum chamber, the silicon substrates were RCA-cleaned: 10 min in H₂SO₄/H₂O₂, followed by a 10% HF dip, then 10 min in NH₄OH/H₂O₂/H₂O, and 10 min in HCl/H₂O₂/H₂O and ultimate HF dip. Subsequently, the native dioxide-free silicon substrates were transported into the deposition chamber through a loading chamber. The sample holder was heated to a temperature of 140 °C monitored by a thermal couple internally equipped. The base pressure of $\sim 2 \times 10^{-4}$ Pa in the deposition chamber was achieved through a combination of rotary and turbo-molecular pumps. Before the deposition, the hydrogen plasma treatment on the substrates was applied for various durations between 0–90 s to investigate the effect of pre-deposition hydrogen plasma exposure on the surface recombination. The flux of silane (H₂) was kept constant at 5 sccm (20 sccm). The inductive RF discharge power was varied between 1.0–2.5 kW. With regards to the characterization of the thin films, the thicker thin films were also deposited on crystal silicon with high resistivity and glass for the measurements of Fourier transform infrared (FTIR)/Raman scattering and UV-VIS transmission spectra, respectively.

The thicknesses of all the deposited thin films were measured directly from the cross-sectional scanning electron microscopy (SEM) image by using a JEOL JSM-6700 F field emission scanning electron microscope. The deposition rate can be calculated from the thickness divided by deposition duration. The high-resolution transmission electron microscopy (HRTEM) measurement was carried out through the use of a JEOL JEM-2010 transmission electron microscope equipped with a 200 kV field emission gun. FTIR and UV-VIS transmission spectra were used to study the Si-H bond

configuration and optical band gap of the samples, respectively. FTIR measurements were performed on a Perkin-Elmer FTIR 1725X spectrometer in the mid-infrared range from 400 to 4000 cm⁻¹ with an increment of 1 cm⁻¹. The Cary 510 Bio spectrometer (300–1100 nm) was used to measure the UV-VIS transmission spectra. The uniformity of the films was examined by mapping the thickness, optical transmission, and resistivity of the samples with diameter of 10 cm. The results show that all the parameters fluctuate well within $\sim 5\%$. The high uniformity of the films is originated from the highly uniform plasma generated in the LFICP reactor. The effective minority carrier lifetime of the double-sided passivated wafer was measured by using the quasi-steady state photoconductance decay (QSSPCD) technique¹⁵ on the facility of WCT-120. The impact of a post-thermal annealing on the surface passivation of a-Si:H/ μ c-Si:H was studied by annealing the lifetime samples in vacuum and H₂ atmosphere in the temperature range of 230–420 °C. The energy conversion efficiency of the solar cell was examined by means of current-voltage (I-V) measurement (Keithley 4200 SCS system) under one sun illumination provided by a standard solar simulator (Peccell PEC-L01).

III. RESULTS

A. Optical band gap and deposition rate

The UV-VIS transmission spectra (shown in Fig. 1) of the thin films deposited on glass at different RF power were measured to extract the parameter of optical band gap E_g . Evident interference fringes due to multi-layer interface reflections were observed in the spectra range longer than the absorption edge. The absorption edge forms a redshift with deposition power, indicating shrinkage of the optical band gap. The transmission T was transformed into absorption α by the relation of $\alpha \propto -\ln(T)$ using the thickness of the films directly read from the cross-sectional SEM images. The optical band gap E_g of a-Si:H/ μ c-Si:H (Si an indirect

FIG. 1. The UV transmission spectra of the thin films deposited at various RF powers on glass substrate. The thickness of the films is in the range of 250–635 nm.

band gap semiconductor) can be deduced from the Tauc equation

$$h\nu\alpha(h\nu) = B(h\nu - E_g)^2, \quad (1)$$

where B is the edge width parameter related to the width of band tails in the film,¹⁶ and $h\nu$ the photon energy. In general, B factor is also taken as a measure of the overall structural disorder and a higher value for B would indicate a lower degree of structure disorder.¹⁷ In our calculation, the obtained value of B ($>800\text{ cm}^{-1/2}\text{ eV}^{-1/2}$) is larger than that in literatures, indicating less disorder and defects in the thin films.

The obtained E_g as a function of applied RF power together with the average deposition rate are both plotted in Fig. 2. A transition point of E_g was observed at power of 1.8 kW. Below 1.8 kW, E_g encounters a decrease from 2.30 eV for 1.0 kW to 2.10 eV for 1.8 kW. On the contrary, E_g increases from 2.10 eV for 1.8 kW to 2.14 eV for 2.5 kW. This changing trend of E_g is related to the crystallinity of the thin films and the hydrogen content, which will be discussed below based on the experiments of Raman scattering and FTIR. The increasing RF power results in the steady increase in the average deposition rate from 7 nm/min to 21 nm/min. These values are about half of those before the modification of the ICP system.¹² We can deduce that there should be a compromise between the deposition rate and the high quality thin film with low level interface defects.

Another feature of the present films is the higher optical band gap E_g than that reported in Refs. 18–20, where the E_g was obtained by the methods other than Tauc method (spectroscopic ellipsometry and surface photovoltage spectroscopy). Although it was recognized that the Tauc method will lead to a larger value for E_g , it will give a correct variation trend of the value with an independent parameter like RF power, substrate temperature, and so on. Herein the values of E_g are above 2 eV, larger than the values ($<1.9\text{ eV}$)¹² obtained in earlier works performed on the direct-plasma ICP system with other similar deposition parameters. This should be correlated to the increased hydrogen content (following FTIR results) in the thin films.

FIG. 2. RF power dependent optical band gap (filled squares) and average deposition rate (filled circles).

B. Raman scattering and crystallinity of the thin films

The micro-Raman scattering experiments were performed to estimate the crystal phase information in the thin films. The obtained spectra are displayed in Fig. 3. It was observed that the dominant peak gradually shifts from $\sim 480\text{ cm}^{-1}$ to $\sim 520\text{ cm}^{-1}$ through a mixed phase state at power of 1.8 kW. This change reflects phase evolution from completely amorphous to almost crystalline with an increasing applied RF power in the films. In fact, the crystallinity value can be estimated by using different methods described in Ref. 21. In this work, the method based on Gaussian line fitting²² is used

$$f_c = (I_c + I_i)/(I_a + I_i + I_c), \quad (2)$$

where I_a , I_i , and I_c are the integrated area of the each phase, i.e., the amorphous ($\sim 480\text{ cm}^{-1}$), intermediate ($\sim 510\text{ cm}^{-1}$) and crystalline phase ($\sim 520\text{ cm}^{-1}$), respectively, in the Raman spectra. A typical deconvolution result is shown in Fig. 4, where the cyan, blue, and green curves (from left to right) denote the amorphous, intermediate, and crystal component, respectively. The experimental (open circle) and overall fitting result agrees well, indicating the validity of the deconvolution procedure. The calculated crystallinity as a function of RF power is included in the inset of Fig. 4. As expected, the crystallinity increases monotonously in the power range of 1.0–2.0 kW because of the production of denser and more energetic ion/radicals in the plasma and area near the surface of the substrate. Higher plasma density means more frequent impacts between the electron and the precursor gases, and thus a larger deposition rate. More energetic ion/radicals imply that the adsorbed radicals on the surface will have a greater diffusion length. This assists the adsorbed radicals to reach the most energetically favorable sites and gives rise to better crystallization of the synthesized thin films.²³ Whereas the crystallinity decreases from 67.0% to 61.6% when the RF power is further increased from 2.0 to 2.5 kW. This should be related to the rapid increase of deposition rate in the range of 2.0–2.5 kW shown in Fig. 2. One possible interpretation may be that: a higher ($>2.0\text{ kW}$) RF power excites more and more precursor ions like SiH, SiH₂,

FIG. 3. The Raman spectra of the thin films deposited at different RF powers.

FIG. 4. Gaussian-shaped curve deconvolution of the Raman spectrum of the thin film deposited at RF powers of 1.8 kW. The inset shows the RF power dependent crystallinity of the thin films.

and SH_3 to improve the growth rate; On the other hand, the over rapid growth minimizes the hydrogen etching effect on the existing weak and strained Si bonds. It is generally accepted that hydrogen etching is also an important mechanism to improve the crystallinity of Si thin films.²⁴

C. FTIR and hydrogen content in the thin films

The FTIR spectra of the thin films deposited with various RF power are shown in Fig. 5. Within wavenumber range of $500\text{--}2300\text{ cm}^{-1}$, three Si-H bond related bands were observed. The first one located at around 640 cm^{-1} was unambiguously attributed to Si-H rocking/wagging mode. Its exact location gradually changed from 644 to 630 cm^{-1} with increasing RF power as displayed in Fig. 6 (the filled circles). This is also correlated to the phase evolution from amorphous to crystal silicon.²⁵ The second one comprising of two sub-peaks located at 845 and 890 cm^{-1} were identified as the bending mode of dihydrides SiH_2 .²⁶ The third one at the region of $\sim 2100\text{ cm}^{-1}$ is recognized as the SiH_x stretching mode. One can see that these hydrogen-related signals become weak with increasing RF power, implying

FIG. 5. FTIR absorption spectra of the thin films deposited at different RF powers.

FIG. 6. The RF power dependent hydrogen content (filled squares) and Si-H wagging/rocking mode location (filled circles).

the decreasing bonded hydrogen content in the thin films. Actually, the bonded hydrogen content in the thin films can be estimated from the Si-H bond rocking/wagging mode using following equation:

$$C_H = A_\omega \int \frac{\alpha(\omega)}{\omega} d\omega = A_\omega I_\omega, \quad (3)$$

where the oscillator strength A_ω is of value of $1.6 \times 10^{19}\text{ cm}^{-2}$.²⁷ The calculated hydrogen content at. % (defined as density ratio of hydrogen to that of hydrogen plus silicon) versus applied RF power is plotted as filled square in Fig. 6. The hydrogen content is in the range of 7.9%–17.4% and exhibits a general decreasing trend with RF power. Meanwhile, much lower values ($< 8\%$) were obtained using the same method in the case of direct plasma.^{12,28} A local fluctuation of hydrogen content was also observed at a power of 1.8 kW, where the thin film is of transition state from amorphous to crystal phase. Further increase in RF power from 2.0 to 2.5 kW leads to a little improvement of hydrogen content, which is consistent with the decreasing crystallinity in this power range shown in Fig. 4.

D. Application in silicon surface passivation

1. Effect of pre-deposition H_2 plasma treatment on surface passivation

a-Si:H/ $\mu\text{c-Si:H}$ thin films with a standard thickness of 50 nm for the study of Si surface passivation were deposited on the *p*-type Si(100) (resistivity of $8\ \Omega\text{ cm}$ and thickness of $600\ \mu\text{m}$) using various RF power. Prior to the deposition, the substrates were treated by H_2 plasma for different duration (0–90 s) to improve the interface properties. The final structure for the minority carrier lifetime measurement is shown in inset of Fig. 7. All the specific minority carrier lifetimes were at an excess of carrier $10^{15}/\text{cm}^3$. The effective lifetime τ values are plotted in Fig. 8 as a function of H_2 plasma treatment time. The τ value is $127\ \mu\text{s}$ without H_2 plasma treatment. The intermediate treatment time (30–60 s) is beneficial to silicon surface passivation, which is evidenced by the improved lifetime value. However, overlong treatment ($> 60\text{ s}$) in H_2 plasma is detrimental to the surface quality,

FIG. 7. RF power dependent minority carrier lifetime (filled squares) and incubation layer thickness (open squares). The inset shows the passivation scheme for the lifetime measurement.

resulting a less lifetime value of 73 μs . The maximum value of carrier lifetime $\sim 230 \mu\text{s}$ was obtained at a time of 30 s. Therefore, in the subsequent experiments, all the substrate will be exposed to H_2 plasma for 30 s just before the passivation layer deposition.

2. Influence of RF power on surface passivation

The RF power dependent effective lifetime τ is shown in Fig. 7. This curve can be separated into three stages: In the first stage (1.0–1.5 kW), τ decreases from 67 to 42 μs ; in the second stage (1.5–2.0 kW), τ rapidly increases from 42 μs to its maximum of 234 μs ; in the third stage (2.0–2.5 kW), τ drops down to 129 μs . Subsequently, the observed pattern of τ will be explained in terms of the properties of the thin films and the interface between the thin film and silicon substrate.

In the above sections, the RF power dependence of the thin film properties were analyzed. It is well known that a low defect state density in the passivation layer will lead to a low defect concentration within it and on the interface between passivation layer and silicon substrate. Therefore, the quality of the a-Si:H/ $\mu\text{c-Si:H}$ is extremely important. In Sec. III A, the factor of B in Eq. (1), an indicative of the defect and disorder within the thin films, was found to have greater values. Additionally, the dark conductivity of the

FIG. 8. The minority carrier lifetime of the sample exposed to H_2 plasma for different time before the passivation layer deposition.

a-Si:H thin films is as low as $\sim 10^{-9} \text{ S/cm}$. Both the high factor B and low dark conductivity imply the low defect density in the thin films.

The low defect density in the thin films is presumably a consequence of hydrogen passivation. As mentioned above, the hydrogen content in these thin films is comparatively larger. However, in the current experiments, the maximum value of τ is obtained at RF power of 2.0 kW, where the corresponding thin film contains the least hydrogen as shown in Fig. 6. Therefore, the change of lifetime τ should not be simply attributed to the change of hydrogen content with the RF power.

Another crucial mechanism to determine the passivation effect is the interface defect between the passivation layer and the substrate. It has been observed that during the deposition of a $\mu\text{c-Si:H}$ layer on top of a substrate, a 30–50 nm thick interlayer referred as “incubation zone”²⁹ is produced. Its crystallinity and thickness strongly depend on the deposition condition and the substrate material. In our experiments, the incubation layer was directly observed in the high magnification cross-sectional SEM images of the deposited thin films on double-side polished Si substrate. Fig. 9 shows the high magnification cross-sectional SEM images of the thin films deposited at power of 1.2 (a), 1.5 (b), 1.8 (c), and 2.0 kW (d). The clear scratches and cracks come from the cross section preparation process. Except of the sample deposited at 2.0 kW, evident incubation layers were observed between the crystal Si films. Furthermore, the thickness of the incubation layers can be determined from the SEM measurement tool by making measurement multiple times at different locations and the results as a function of RF power are plotted in Fig. 7 (the open squares). The error bars shown in Fig. 7 represent the standard deviations from the mean thickness values from the multiple metering. At a power of 1.5 kW, the thickness has a maximum of $80 \pm 7 \text{ nm}$ (>the standard passivation layer thickness of 50 nm), while the lifetime τ has a minimum of 42 μs . No evident incubation layer was observed at the power of 2.0 kW, at which the greatest

FIG. 9. The cross-sectional SEM images of the thin films deposited at RF power of 1.2 kW (a), 1.5 kW (b), 1.8 kW (c), and 2.0 kW (d). Evident incubation layers were observed at the interfaces.

minority lifetime value was obtained. Linking the curve of incubation with that of the lifetime, one will find that the incubation layer thickness changes with the RF power in an opposite way to the minority carrier lifetime τ dose. This observation suggests the fact that the incubation layer on the interface between the passivation layer and crystal Si will worsen the passivation effect of the a-Si:H/ μ c-Si:H thin films.

The CVD deposition of Si thin films involves a complex combination of several processes including the arrival and removal of gas molecules or precursors at the substrate surface, the decomposition into reactive species, and the migration of these species on the surface where they can lead to nucleation and continued deposition.³⁰ The adsorbed reactive species are likely to come to rest when a position of minimum energy position is found. The minimum energy position can be a defect at the substrate surface, which will result in a new nucleus or an existing nucleus.³¹ At a certain process condition, the formation of nuclei will be delayed for some time known as the incubation time.³⁰ From the point view of a growth mechanism, the incubation layer (initial growth) will be rich of defects, which will lead to the intense recombination of the photon-induced carriers and thus a decreasing lifetime value observed in Fig. 7.

3. Influence of thermal annealing on surface passivation

In order to investigate the influence of the post-deposition annealing on the silicon surface, the samples were thermally annealed in vacuum and H₂ flow atmosphere. For simplicity, one sample with an as-deposited lifetime value of 196 μ s was annealed just in vacuum in the temperature range of 230–500 °C. Fig. 10 shows the evolution of lifetime τ with annealing temperatures. The annealing duration at each temperature point is 30 min. One can see that the lifetime increases almost linearly in the range of 230–420 °C. Further increasing annealing temperature to 500 °C results in a significant decrease in lifetime. The low temperature (<500 °C) annealing in vacuum leads to the lifetime improvement by a factor of about 2.5. The corresponding FTIR transmission spectra of the sample before and after thermal annealing were measured in the wavenumber range of 550–950 cm⁻¹

FIG. 10. The minority carrier lifetime of the sample annealed at different temperatures in vacuum.

to clarify the H role in the surface passivation. The results of the as-deposited and annealed at temperature at 420 and 500 °C are exhibited in Fig. 11. The Si-H wagging/rocking mode at about 630 cm⁻¹ changes slightly with temperature increasing from 230 to 420 °C. In comparison, this mode considerably recedes when temperature is increased from 420 to 500 °C, which is indicative of lower hydrogen content after annealing. The mode around 850–900 cm⁻¹ also becomes weak after annealing at a temperature of 420 and 500 °C.

The above vacuum annealing results represent the important role of hydrogen atom in the Si surface passivation. Low temperature (<420 °C) annealing enables the diffusion of hydrogen in the thin film toward the Si substrate, which effectively reduces the dangling bond density at the interface³² and enhances the minority carrier lifetime. At higher temperatures (>420 °C), hydrogen atom effuses outside of the samples, leading to the re-generation of the dangling bonds and thus decreasing in the lifetime value.

Systematic annealing experiments were performed on the samples deposited at different RF powers and the ultimate lifetime values (not shown here) presented the same trend with that of as-deposited samples shown in Fig. 7 (filled squares). These results show that the as-deposited interface features, especially the incubation layer properties discussed above, are the crucial factors in determining the ultimate lifetime values in our case. Therefore, we will focus on the sample with the highest as-deposited lifetime value. Fig. 12 exhibits the lifetime value evolution with annealing time at 420 °C in vacuum (filled squares) and H₂ flow (filled circles). In the case of vacuum annealing, the lifetime value increases sharply in the initial 95 min and saturates at the value of 421 μ s at about 185 min. On the contrary, the lifetime reaches the maximum of 524 μ s in a short time of 11 min in the case of H₂ flow. It seems that the presence of hydrogen in the annealing atmosphere is essential to improve the level of surface passivation for our a-Si:H/ μ c-Si:H thin films, despite the presence of rich hydrogen in the film as evidenced by the FTIR result. Therefore, the H₂ atmosphere annealing is time-saving from the solar cell fabrication process point view.

FIG. 11. The FTIR transmission spectra (550–950 cm⁻¹) of the as-deposited sample and that annealed at 420 °C and 500 °C. Increase in the annealing temperature from 420 °C to 500 °C leads to the decreasing hydrogen content in the film.

FIG. 12. The minority carrier lifetime as a function of annealing duration at 420 °C at atmosphere of vacuum (filled squares) and H₂ flow (filled circles).

4. Injection level dependent surface recombination

The effective minority carrier lifetime τ_{eff} is correlated with the effective surface recombination velocity S_{eff} through the following equation:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S_{eff}}{d}, \quad (4)$$

where τ_{bulk} is the bulk lifetime, S_{eff} the effective surface recombination velocity, and d the sample's thickness. By neglecting the bulk lifetime ($\tau_{bulk} \rightarrow \infty$), we can get the maximum value of the surface velocity from this equation. The injection level dependent S_{eff} with and without annealing is plotted in Fig. 13. Comparing the result of the as-deposited and annealed, one can see that the low temperature annealing leads to the decreasing of the surface recombination especially in the range of the low injection levels. The as-deposited sample has a surface recombination of about 150 cm/s. The annealing at 230 °C for 11 min results in the decreasing of S_{eff} above the injection level of $1 \times 15/\text{cm}^3$ and increase of S_{eff} below the same level. This abnormal increase in S_{eff} possibly stems from the excitation of the adsorbed atoms in the circumstance, which acts as the additional recombination centers to deteriorate the lifetime value. Subsequent annealing at increasing temperatures causes the continuous decreasing towards the injection level of $2.8 \times 16/\text{cm}^3$, where the Auger recombination plays a dominant role and the curves tend to

FIG. 13. The injection level dependent surface recombination velocity of the as-deposited sample and that annealed at different temperatures.

converge. At the temperature of 420 °C, the lowest surface recombination velocity is 60 cm/s at the injection level of $1 \times 15/\text{cm}^3$. It should be emphasized that this S_{eff} value is the upper limit because of the adopting of an infinity assignment for the bulk lifetime.

IV. DISCUSSIONS

A. The high as-deposited lifetime values

As far as we know, the present *as-deposited* lifetime value of 234 μs is much higher than that reported in literatures, where capacitively coupled plasma CVD or HWCVD methods were used to deposit the passivation layer of a-Si:H/ $\mu\text{c-Si:H}$. Willem *et al.*³³ summarized the passivation effects of a-Si:H deposited by various methods and the following as-deposited lifetime values of Fz silicon substrate were obtained: 34 μs for PECVD, 43 μs for VHF PECVD, and 87 μs for HWCVD. As mentioned above, the passivation can be physically divided into two types: hydrogen-related chemical passivation and built-in potential related field passivation. From the point view of field passivation, the a-Si:H/ $\mu\text{c-Si:H}$ thin films has the wider band gap than crystal silicon substrate, which will form a barrier for photogenerated carriers and restrain the carrier recombination through surface dangling bonds. As shown in Fig. 2, present a-Si:H/ $\mu\text{c-Si:H}$ has wide optical band gaps in the range of 2.1–2.3 eV. It is well known that the Tauc method may lead to an overestimated optical band gap value. However, this will not qualitatively influence the barrier nature of the passivation layer. If the high as-deposited lifetime value is principally attributed to the band offset between the passivation layer and the crystal silicon substrate, the different changing trends of lifetime and optical band gap with RF power cannot be explained. Therefore, it should be correlated with the hydrogen related chemical passivation.

It has been shown that the pre-deposition hydrogen plasma exposure significantly influences the surface passivation (see Fig. 8). In the post-deposition annealing, the interaction between hydrogen atom from the passivation layer and the c-Si substrate is crucial to the surface passivation. Mitchell *et al.*³⁴ studied the thermal activation of the hydrogen related chemical passivation on silicon substrate and determined the thermal activation energy of E_A through the following formula:

$$1/\tau_{reac} = A \exp(-E_A/k_B T), \quad (5)$$

where τ_{reac} is the reaction time between hydrogen and silicon, E_A activation energy of surface passivation, k_B the Boltzmann constant, and T the temperature. According to Eq. (5), a low E_A value will point to a high reaction rate $1/\tau_{reac}$ or a short reaction time τ_{reac} . In earlier works,^{12,23} we have analyzed the effect of high-density hydrogen plasma from the LFICP source on the crystallinity of deposited $\mu\text{c-Si:H}$ thin films. Abundant atomic hydrogen resulted from the dissociation of SiH_4 and H_2 will result in high surface coverage by hydrogen, which reduces the activation energy E_A and the reaction time τ_{reac} . In addition, high-density hydrogen can produce effective local plasma heating via the hydrogen recombination on the

growth surface: $\text{H} + \text{Si} - \text{H} \rightarrow \text{Si} \cdot + \text{H}_2$, with the dangling bond $\text{Si} \cdot$. In other word, the chemical annealing during the deposition improves the lifetime to a considerable value within the deposition process even without any additional thermal-annealing.

B. Incubation layer and control of incubation layer thickness

Fig. 14(a) [(b)] shows a low- (high-) magnification cross-sectional TEM micrograph of LFICP-grown $\mu\text{c-Si:H}$ on silicon substrate. In Fig. 14(a), clear incubation layer (dark area) between the film and substrate is discriminated like in SEM images. Fig. 14(b) exhibits more details of the interface. The grey area in the film corresponds to the microcrystalline Si fractions, which are conical conglomerates of microcrystals. As observed above, the incubation layer is detrimental for the improvement of lifetime and its thickness is highly dependent on the process parameters, e.g., the applied RF power in our case. So, a deep understanding on the mechanism to control the formation of incubation layer is extremely important. It was recognized that the ion bombardment played a crucial role in the formation of incubation layer in Ref. 35. The ion beam works in two possible ways: (i) a surface effect: very small grains do not survive the high dose of ion irradiation, thereby reducing the nucleation rate and (ii) a bulk effect: the ion beam induces defect-related grains growth. On this basis, two strategies³⁵ to control the ion beam were proposed: the choice of the frequency of the power source generating the plasma, and the design of the electrode configuration to avoid its formation. In our case, the ions/electrons energy is around several eVs, below the threshold value of 16 eV for defect formation for Si. Therefore, the modified LFICP system makes it possible to minimize the effect of the ion bombardment to a very low level.

From the point view of a growth mechanism, the key of the diminishment of the initial growth of incubation layer seems to lie in the rapid nucleation without retard on the interface. In our case, this occurs at the power of 2.0 kW, near the transition point (1.8 kW) from a-Si:H to $\mu\text{c-Si:H}$. This is consistent with other authors' findings that the good passivation is obtained with passivation layers deposited close to microcrystalline regimes, where the depletion fraction of SiH_4 is comparatively higher than that of amorphous regimes.^{2,36} In the current study, although the silane depletion was not experimentally measured at certain RF power, the high depletion fraction at the power of 2.0 kW is reason-

ably speculated. The detailed relation between the depletion fraction and the incubation time in the growth of a-Si:H/ $\mu\text{c-Si:H}$ need to be further clarified in future work.

It was recognized that the passivation effect of the intrinsic a-/ $\mu\text{c-Si:H}$ thin films is strongly dependent on its thickness. In a practical Si-based HT solar cell, both the front and the rear passivation layer is of the thickness of about several nanometers. This is because thicker passivation layer possibly results in more light loss and undesirable energy barrier for electrical transport and thus decreases the energy conversion efficiency of the solar cell. Therefore, the passivation effect of the a-/ $\mu\text{c-Si:H}$ thin films with device-grade thickness is particularly meaningful to a high efficiency HT solar cell. In order to examine the applicability of present a-/ $\mu\text{c-Si:H}$ thin films for surface passivation in a practical HT solar cell, a solar cell with core structure of $\text{ZnO:Al}/\mu\text{c-Si:H}$ (*n*)/ $\mu\text{c-Si:H}$ (*i*)/C-Si (*p*) was fabricated using the same LFICP setup. Prior to the deposition of the passivation layer, the substrate (with resistivity of $\sim 2 \Omega \text{ cm}$ and thickness of $\sim 300 \mu\text{m}$) was treated in H_2 plasma for 30 s to improve the interface properties. The intrinsic layer with thickness of about 8 nm was deposited at the optimum discharge power of 2.0 kW. The PH_3 gas was used as the dopant source for the synthesis of the *n*-doped layer (of thickness of $\sim 12 \text{ nm}$). The top ZnO:Al layer, front grid, and rear sheet aluminum electrodes were deposited using magnetron sputtering. The fabricated solar cell was annealed at 420°C in H_2 flow for 10 min. The dark and illuminated I-V curves of the fabricated HIT (Heterojunction with Intrinsic Thin Layer) solar cell are shown in Fig. 15. As seen from the dark I-V, the solar cell displays an electrical transport mechanism described by the double-diode model.³⁷ Under one sun illumination, the solar cell exhibits a excellent performance: open voltage (V_{oc}) of 583 mV, short circuit current density (j_{sc}) of 32.3 mA/cm^2 , fill factor (*FF*) of 64%, and the total energy conversion efficiency (η) of 12.1%. Indeed, these results are lower than current record photovoltaic parameters of HIT solar cell reported in Ref. 38 due to the oversimplified structure. In present solar cell, the silicon surface is flat without any chemical texture, and double-sided passivation used in Sanyo's HIT solar cell is not involved. These deficiencies will limit its photovoltaic performance as expected.

FIG. 14. A typical cross-sectional TEM micrograph of LFICP-grown $\mu\text{c-Si:H}$ films on Si substrate at low (a) and high (b) magnification.

FIG. 15. The dark and illuminated I-V curves of the heterojunction solar cell with a forward intrinsic silicon passivation layer deposited at discharge power of 2.0 kW using the LFICP method.

However, the present result promises a new way other than the conventional PECVD to Si:H deposition for Si surface passivation and HIT solar cell applications.

V. CONCLUSIONS

In summary, high quality a-Si:H/ μ c-Si:H thin films were deposited using a modified LFICP source at various RF powers at low temperatures. The bulk properties such as the optical band gap, the crystallinity, and the bonded hydrogen content in the thin films showed interesting transitions near the phase-change region from amorphous to microcrystalline. These thin films displayed deposition-power dependent passivation effects on crystal silicon. The underlying mechanism was analyzed in terms of the bulk properties of the passivation layer and the interface features between the a-/ μ c-Si:H film and silicon substrate. It was found that the incubation layer significantly influences the passivation effect assessed by carrier lifetime measured by QSSPCD method. A well passivation effect was obtained with short or zero incubation time in the initial growth before the nucleation presence. Proper pre-deposition hydrogen plasma exposure is beneficial to the lifetime improvement. High-density hydrogen related chemical annealing leads to the high as-deposited lifetime values without any additional annealing. The post-deposition thermal annealing can also enhance the lifetime value through hydrogen diffusion toward to the interface to reduce the interface defects. The injection level dependent surface recombination velocity at different annealing temperature was also deduced and the lowest value at carrier density of $1 \times 10^{15} \text{ cm}^{-3}$ was 60 cm/s. The applicability of the silicon thin films grown by LFICP method for passivation in practical HT solar cells was verified by the excellent photovoltaic property of the HT solar cell.

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