Control of epitaxial growth at a-Si:H/c-Si heterointerface by the working pressure in PECVD*

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(Received 30 May 2016; revised manuscript received 17 July 2016; published online 28 September 2016)

The epitaxial-Si (epi-Si) growth on the crystalline Si (c-Si) wafer could be tailored by the working pressure in plasma-enhanced chemical vapor deposition (PECVD). It has been systematically confirmed that the epitaxial growth at the hydrogenated amorphous silicon (a-Si:H)/c-Si interface is suppressed at high pressure (hp) and occurs at low pressure (lp). The hp a-Si:H, as a purely amorphous layer, is incorporated in the lp-epi-Si/c-Si interface. We find that: (i) the epitaxial growth can also occur at a-Si:H coated c-Si wafer as long as this amorphous layer is thin enough; (ii) with the increase of the inserted hp layer thickness, lp epi-Si at the interface is suppressed, and the fraction of a-Si:H in the thin films increases and that of c-Si decreases, corresponding to the increasing minority carrier lifetime of the sample. Not only the epitaxial results, but also the quality of the thin films at hp also surpasses that at lp, leading to the longer minority carrier lifetime of the hp sample than the lp one although they have the same amorphous phase.

Keywords: hydrogenated amorphous silicon (a-Si:H), epitaxial growth, interface, plasma-enhanced chemical vapor deposition (PECVD)

PACS: 88.40.H–, 78.55.Qr, 77.55.Px, 73.40.Kp **DOI:** 10.1088/1674-1056/25/11/118801

1. Introduction

In Si-based solar cells, the highest open circuit voltage (V_{oc}) (750 mV) and cell efficiency (25.6%) have been achieved by the hydrogenated amorphous silicon (a-Si:H)/crystalline Si (c-Si) heterojunction structure using a-Si:H to passivate symmetrically both sides of the c-Si wafer (so-called HIT solar cell).[1,2] One of the key factors for the high performance of the HIT solar cell is that there is no epitaxial growth at the a-Si:H/c-Si interface, which improves the surface passivation and junction properties.[3,4] Unfortunately, an epitaxial layer is formed rather easily at the a-Si/c-Si interface during the plasma-enhanced chemical vapor deposition (PECVD), even without the presence of H_2 gas.[5] It has been widely accepted that this epitaxial Si (epi-Si) is detrimental to solar cells since it includes many structural defects, such as H-related defect complexes, resulting in a low minority carrier lifetime.[6,7] But some researchers argued that the epi-Si growth is not always harmful and sometime even beneficial to the performance of the devices.[8–10] It was proposed that epitaxial growth is of two types:[8] (i) an epitaxial layer with a sharp interface and (ii) a mixed phase of crystalline and amorphous materials, and the presence of the former will not cause the loss in V_{oc} but the latter must be suppressed to achieve high efficiencies in a-Si:H/c-Si solar cells. Very recently, it was reported that a high lifetime of over 7 ms was achieved in an intrinsic hydrogenated amorphous silicon oxide (a-SiO_x:H) passivated c-Si wafer when the epitaxial phase was present.[9] A simple control of process for the epitaxy on the c-Si surface is necessary to apply or avoid this special phase microstructure in heterojunction solar cells.

The epi-Si growth often occurs at high substrate temperature, low power, and high H_2 dilution.[11] For instance, Fujiwara *et al.* found that the intrinsic a-Si:H layer is partially epitaxial at the temperature of over 140 °C and becomes completely epitaxial at temperature higher than 180 °C. It was also reported that epitaxial growth was suppressed at high working pressure.[6] The working pressure involves the silane depletion fraction, radical interaction probability, electron density, surface diffusion, and mean free path of generated radials from the plasma.

In this work, pure a-Si:H layer on c-Si substrate is achieved at high pressure (hp) and epi-Si layer at low pressure (lp), both thin films on Si wafer, glass, and a-Si:H/c-Si substrates have been investigated by spectroscopic ellipsometry (SE) and Sinton WCT-120 effective lifetime measurement setup. Especially SE, as a rapid, noncontact optical technique, plays an importance role for measuring the dielectric function, the film thickness, and the film crystallinity using the

*Project supported by the Natural Science Foundation of Hebei Province, China (Grant No. E2015201203) and the International Society for Theoretical Chemical Physics of China (Grant No. 2015DFE62900).

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Tauc–Lorentz method combined with the Bruggeman effective medium approximation (BEMA) model. To study the effect of the initial stage of the thin film growth on the epi-Si growth, a hp pure a-Si:H layer is incorporated between the lp a-Si:H layer and the c-Si substrate, as stated above, the epi-Si growth at lp should plausibly be prevented. However, the lp epitaxial growth is avoided only when the thickness of the hp layer is up to 9 nm while failing to suppress when it is $<\sim$ 3.6 nm, which implies epi-Si can also occur at the a-Si:H coated c-Si wafer surface as long as this amorphous layer is thin enough. For further confirmation, the structural compositions and the minority carrier lifetimes of some stack schemes as functions of the thickness of the hp amorphous layer are also evaluated.

2. Experiment

280 μm-thick (100)-oriented boron-doped float zone (FZ)-Si wafers (1–5 Ω·cm) with double-side polished (DSP) surfaces were used as the substrate materials. The high quality of the FZ-Si wafer allows us to neglect the contribution of the bulk to the total recombination, and the DSP mirror surface eliminates the influence of the wafer surface roughness on the passivation properties and allows the application of SE measurements. The samples were dipped in HF solution (5%, 3 min) to remove the native oxide layer, and then immediately transferred to the chamber of a cluster-PECVD system for the deposition of a-Si:H film to achieve symmetrical passivation on both sides of the c-Si wafers. Glass (Schott AF 32^{TM}eco) substrates always accompanied each side of the wafer as a reference. The details of the deposition conditions are provided in Table 1.

Table 1. Deposition condition of a-Si:H thin films.

Frequency	13.56 MHz
Electrode distance	19 mm
Excitation power	4 W
Gas ratio (SiH_4:H_2)	1:4.5
Temperature	175 °C
Pressure	0.5–1.5 Torr

The kinetics of material growth is often related to the deposition rate (R_d).[12] In this study, to reduce this effect, two deposition conditions with similar R_d but very different working pressures were adopted although they had different plasma chemistry and species.[13] Figure 1 shows the variation of R_d for the a-Si:H thin film grown on glass with the pressure, from which we can see that R_d increases first and then decreases with the increase of the working pressure. R_d at 0.5 Torr is almost equal to that at 1.2 Torr, hence, these two process points are preferred for the lp epitaxial layer and the hp non-epitaxial layer (this will be confirmed in the following) to facilitate this study. It should be pointed out that although the other parameters are kept the same for several designed groups in this study except for the pressure, hp and lp are relative, the pressure effect on the material properties might be different when other parameters or tools are introduced.

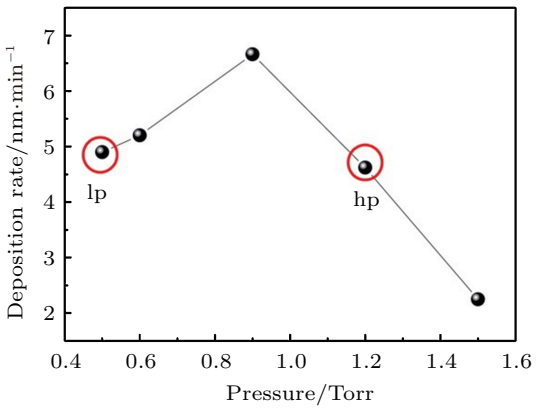


Fig. 1. (color online) The deposition rate as a function of the working pressure.

The epitaxial growth of a-Si:H thin films on c-Si was analyzed by an UV–visible SE (Horiba JobinYvon UVISEL spectroscopic ellipsometer, using a 70° fixed incidence angle). SE is a powerful optical diagnostics technology commonly used to characterize Si-based thin films, and measures the change in the polarization of light upon reflection from a surface and provides information on the linear optical properties, thickness, and surface roughness of the films and substrates.[14,15] Especially its application to characterize the formation of fully epitaxial Si and the breakdown of epi-Si into mixed phase material has been systematically studied in theory[16–18] and confirmed in experiment by the transmission electron microscopy (TEM).[4,6,8,19] The optical properties from SE, as represented by the imaginary part of the dielectric function, provide a clear indication of the crystalline growth and allow the quantification of crystallinity, voids, density, and even hydrogen content of the thin films.[16] The model is important for accurate analysis in SE measurement. In this paper, three models have been built as shown in Fig. 2. The crystallinities of all thin films on glass substrates were detected by Raman scattering spectroscopy.[20,21] The bonding configuration within the films was characterized by Fourier transform infrared (FTIR) absorption spectra. Minority carrier lifetime (lifetime) measurements were conducted by the Sinton WCT-120 effective lifetime measurement setup and lifetime was given at a constant minority carrier density of 10^{15} cm^{-3}.

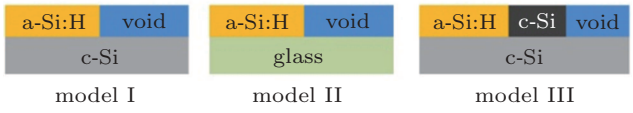
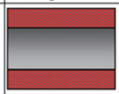
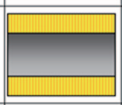
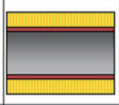


Fig. 2. (color online) Models used to analyze SE data of samples in this work.

3. Results and discussion

After the lp, hp, lp/hp (3.6 nm), and lp/hp (9.0 nm) deposition, a yellowish silicon layer can be easily found on the glass substrate. SE fitting based on model II (a-Si:H layer on glass) yields a thickness of around 50 nm for the four samples (as can be seen in Table 2). The good fitting, indicated by the small fitting parameter χ^2 (the squared difference between the measured and the calculated values of the SE parameters), implies the suitability of model II. As shown in Table 2, the lifetime of the hp a-Si:H thin film passivated c-Si wafer can reach 1.15 ms. The thickness of the hp a-Si:H thin film can be obtained by fitting the SE curves based on model I (only a-Si:H composition in thin film layer). For the lp a-Si:H thin film, however, it is completely different. No color change can be seen from the c-Si wafer after the silicon film deposition. The lifetime of the lp silicon film layer coated wafer is only 68 μs and close to that of wafers without surface passivation layer (about 40–60 μs after wet chemical cleaning). Likewise, the SE fit based on model I does not give an effective thickness. However, a 58.9 nm thick a-Si:H layer is deposited on the accompanying glass substrate, which suggests that silicon deposition on the c-Si substrate is also very likely. In addition, the SE fit based on model III (including c-Si composition) provides a thickness of 38.6 nm with a decent fitting parameter. This in turn suggests that the lp a-Si:H thin film on c-Si wafer may undergo epitaxial growth, and is not pure amorphous, which results in bad passivation; hp could suppress epitaxy leading to a long lifetime. Note here lp a-Si:H on c-Si wafer is actually not amorphous due to the presence of epitaxy, so a square bracket is used to define the nominal a-Si:H, i.e., lp [a-Si:H].

Table 2. Site experiment observations and measurements.

Thin films	Schematic figures	Lifetime (Sinton)	Color change	SE thickness (the model)
hp		1.15 ms	Yes/c-Si Yes/glass	36.1 nm/c-Si (I or III) 46.2 nm/glass (II)
lp		68 μs	No/c-Si Yes/glass	0.7 nm/c-Si (I) 38.6 nm/c-Si (III) 58.9 nm/glass (II)
lp/hp (3.6 nm)		171 μs	No/c-Si Yes/glass	0.9 nm/c-Si (I) 43.7 nm/c-Si (III) 55.4 nm/glass (II)
lp/hp (9.0 nm)		663 μs	Yes/c-Si Yes/glass	47.8 nm/c-Si (I or III) 50.8 nm/glass (II)

a-Si:H(i) at high pressure
a-Si:H(i) at low pressure
c-Si

Further, we attempt to incorporate the hp a-Si:H layer in the lp a-Si/c-Si interface to prevent the epitaxial growth of lp [a-Si:H] on c-Si. In this case, the total thickness of the passivation layer is always kept to be similar from sample to sample. The incorporation of the ∼3.6 nm-thick hp a-Si:H layer brings about a little increase of the lifetime (171 μs), but the thickness fit of the thin films is still the same as the lp [a-Si:H] thin film directly grown on c-Si, i.e., model III, rather than model I, has provided an effective thickness. It indicates that the epitaxial growth still occurs, which may be attributed to the hp layer being too thin to separate the interaction of c-Si surface energy with radicals dropped to the surface of c-Si from plasma.[22] When a 9 nm hp layer is applied to the lp a-Si:H/c-Si interface, the lifetime of the sample increases to 663 μs dramatically, and the thickness of the thin film can be presented by model I which just includes the amorphous phase, implying that the epitaxial growth has been suppressed. Note that the lifetime is not equal to that of the sample with the complete hp layer, and the reason will be unraveled hereinafter.

Raman spectra and dielectric functions from SE are employed to demonstrate the crystallinity of these samples in Table 2. First, four sets of thin films grown on glass substrates are evaluated with Raman spectra, as shown in Fig. 3. They are obviously purely amorphous because only one Raman peak at 480 cm^{-1} is detected corresponding to the amorphous phase. This can be ascribed to low H_2 dilution (SiH_4:H_2=1:4.5) which is a process window of the amorphous phase. Figure 4(a) shows the imaginary part of the pseudodielectric of the thin films on c-Si wafers. The sharp peaks of the samples with lp [a-Si:H] and lp/hp (3.6 nm) [a-Si:H] thin films start to appear near 3.4 eV and 4.2 eV, suggesting epitaxial growth at the interface; and only a single peak of the samples with hp a-Si:H and lp/hp (9 nm) a-Si:H is presented at around 3.7 eV, demonstrating that a complete amorphous phase is obtained and the epitaxial growth is suppressed. Figure 4(b) also presents the dielectric function curves of the four thin films grown on glass substrates, corresponding to the samples of Raman measurements. The shape and the position of the main peaks are fully the same as those of amorphous phase samples in Fig. 4(a), which is consistent with the Raman analysis. The inset in Fig. 4(a) is the imaginary part of the dielectric function for the hp a-Si:H thin layer with a thickness of < 25.6 nm. When the thin films are very thin, the peak depression occurs around 3.7 eV. This could be attributed to the contribution of the signal from the c-Si substrate. But this situation is different from that of epi-Si.[6] With the increase of the thickness of the thin layer, the substrate effect is cut off, and the peak of 3.7 eV is completely presented, indicating that these thin films are amorphous.

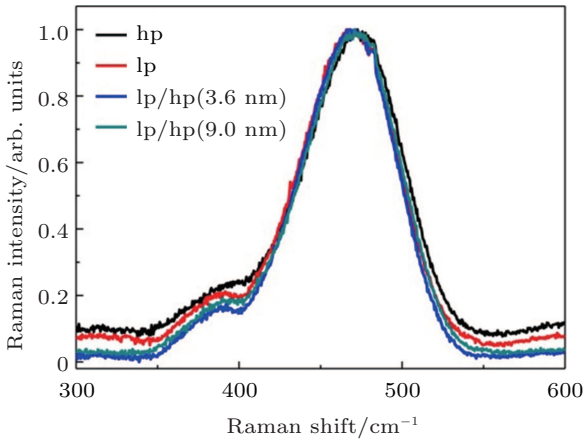


Fig. 3. (color online) Raman spectra of thin films on glass substrates.

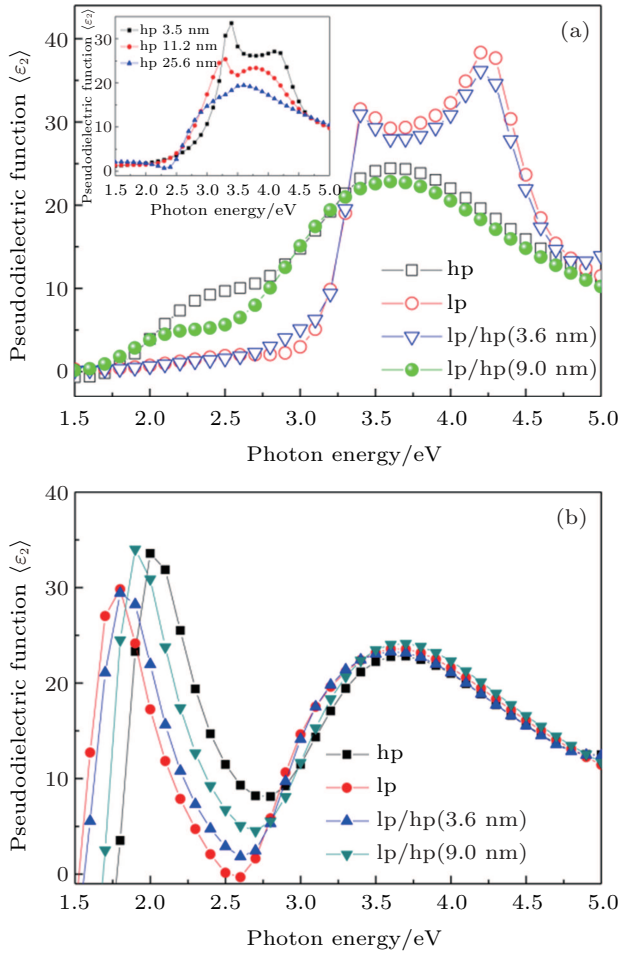


Fig. 4. (color online) Imaginary part of the dielectric function for thin films on (a) silicon wafer substrates and (b) glass substrates. The inset is the imaginary part of the dielectric function for the hp a-Si:H thin layer with different thickness.

Test data suggests that lp and lp/hp (3.6 nm) thin films are epitaxially grown on c-Si wafer, i.e., a lot of and even all crystalline phase has been shaped in thin films, so model III is the best choice for the SE fit (including the data in Fig. 4(a)), from which the precise R_d of the lp epi-Si layer on c-Si wafer is obtained. Figure 5 presents R_d information of the thin films on c-Si and glass substrates at hp and lp. We find that R_d of the thin films on glass substrates is more or less the same, while on c-Si, R_d of the hp thin film is larger than that of the lp thin film due to the presence of the epitaxial layer. As the hp layer is inserted at the lp layer/c-Si interface, the initial growth stage of the lp thin films changes from the surface of the c-Si wafer to that of the hp a-Si:H thin film. With the increase of the thickness fraction of the inserted hp a-Si:H layer, R_d begins to increase and eventually tends to the same with R_d on the glass substrate owing to the suppression of epitaxial growth. These remind us to pay attention to the influence of the instant change of the initial surface on R_d during thin film growth in the a-Si:H/c-Si heterojucntion, especially for the fabrication of the doped a-Si:H thin film as emitter or back field, it is closely related to the thickness and crystallinity of the intrinsic layer for the fabrication of HIT solar cells.

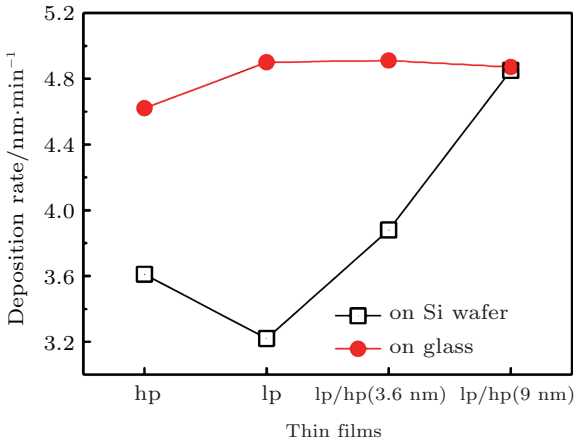


Fig. 5. (color online) The deposition rates of the thin films on different substrates at high pressure and low pressure.

The SE analysis based on model III also provides the structural fractions (percentage) of c-Si, a-Si:H, and void in the thin film. We use the thickness of the hp layer (d_{hp}) divided by the total thickness of the hp layer and the lp layer ($d_{hp}+d_{lp}$) as abscissa and plot the curves about the structural percentages of c-Si, a-Si:H, and void in the thin film as a function of $d_{hp}/(d_{hp}+d_{lp})$, as shown in Fig. 6(a). It is found that the fraction of the a-Si:H phase increases and that of the c-Si phase decreases with the increase of $d_{hp}/(d_{hp}+d_{lp})$, while the fraction of void first increases and then decreases. Figure 6(b) gives the lifetime and the implied V_{oc} measured by a Sinton instrument as a function of $d_{hp}/(d_{hp}+d_{lp})$, from which the similar trend with the above can be seen. In addition, only the 8.5 nm hp layer passivated wafer also shows the lifetime of 135 μs and the implied V_{oc} of 620 mV (not shown here), which is superior to the results of the epitaxial layer passivated one. It seems to explain why the epitaxial growth is prevented with the increase of the inserted hp layer thickness. In Fig. 4(a), we already know that the dielectric function curves for hp and lp/hp (9 nm) thin films on c-Si substrates are almost the same, indicating that the epitaxial growth for these two thin films

has been completely suppressed, but the lifetime and the implied V_{oc} of the thin films passivated c-Si wafers still have big differences. It can be concluded that the passivation effect depends on not only whether the epitaxial growth happens or not at the a-Si:H/c-Si interface, but also the quality of the a-Si:H thin film itself. The change of void fraction in Fig. 6(a) plausibly reveals this point. Firstly, the fraction of void in lp and lp/hp (3.6 nm) [a-Si:H] is less than that in hp and lp/hp (9 nm) a-Si:H. This is because epitaxy happening reduces the composition of a-Si:H in which microstructures of voids exist.[23] Secondly, also in the amorphous phase, the fraction of void in lp/hp (9 nm) a-Si:H is more than that in hp a-Si:H, indicating that lp a-Si:H has worse film quality than hp a-Si:H. It was reported that voids in a-Si:H were concerned with SiH_2 bonding.[13] FTIR absorption spectra are measured to calculate the Si–H_2/Si-H ratio, which is done by analyzing Si-H and Si-H_2 modes near 2000 cm^{-1} and 2100 cm^{-1}, respectively. It is obtained that the Si–H_2/Si-H ratio is 5.5% in hp a-Si:H and 12% in lp/hp (9 nm) a-Si:H, which confirms the results above.

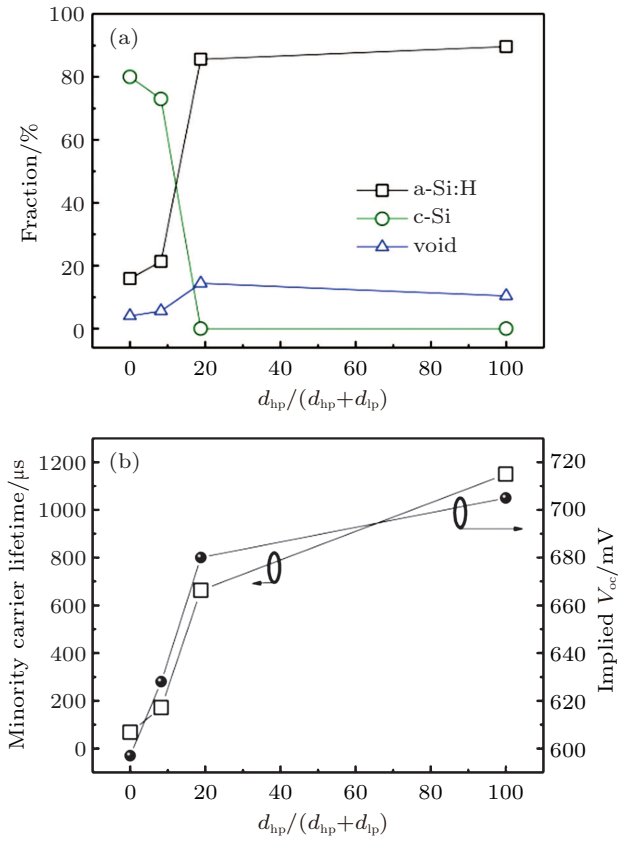


Fig. 6. (color online) (a) The fractions of c-Si, a-Si:H, and void in the thin film and (b) the lifetime and implied V_{oc} as a function of $d_{hp}/(d_{hp}+d_{lp})$.

We can draw a conclusion that hp not only suppresses the epitaxial growth, but also presents a high quality a-Si:H film on c-Si substrate, and lp results in the epi-Si easily. Even if no epitaxial growth occurs (e.g, in this study, epitaxial growth has been avoided by the incorporation of a 9 nm hp layer), lp a-Si:H also does not possess the best film quality and hence lp is not suitable to be used for passivating c-Si wafer in a-Si:H/c-Si heterojunction solar cells. It is still a question of why the working pressure can affect the epitaxial growth and the thin film quality? It is known that hp would increase the number of ionization events and silicon radicals colliding, leading to the increase of the electron density and the decrease of the electron temperatures, which favor the volume reaction rather than the surface reaction because of the reduction in the mean free path of the generated radials in the plasma.[4] The hp also accomplishes more silane depletion and the lower void fraction inside the film with moderating hydrogen content. It was reported that the atomic hydrogen can react with the silane network and terminate dangling bonds and remove weak bonds, and hp contributes to hydrogen dominating the film.[19,24] In addition, the ion bombardment becomes weaker at hp, favoring the growth of high quality films.[6]

4. Conclusion

A fruitful investigation is provided for confirmation that the control of the epitaxial growth status of a-Si:H thin film can be achieved by the working pressure in PECVD technology. The millisecond lifetime can be obtained at high working pressure due to suppression of epi-Si growth. The thin film with high quality, such as less voids and high density, can also be obtained at high pressure. While at low pressure, the low quality of thin film and the poor passivation effect are yielded because of the presence of epi-Si. In lp epi-Si/c-Si samples, the incorporation of a hp layer at the interface can prevent epitaxial growth unless the thickness of this layer is too thin. As the thickness of the hp layer increases, the lp thin film tends to amorphous phase thoroughly, generating the increase of the lifetime and the implied V_{oc}. All detailed studies pave the way for epistemology in HIT solar cell industrialization.

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