# Interface states study of intrinsic amorphous silicon for crystalline silicon surface passivation in HIT solar cell*

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Intrinsic hydrogenated amorphous silicon (a-Si:H) film is deposited on n-type crystalline silicon (c-Si) wafer by hot-wire chemical vapor deposition (HWCVD) to analyze the amorphous/crystalline heterointerface passivation properties. The minority carrier lifetime of symmetric heterostructure is measured by using Sinton Consulting WCT-120 lifetime tester system, and a simple method of determining the interface state density ($D_{it}$) from lifetime measurement is proposed. The interface state density ($D_{it}$) measurement is also performed by using deep-level transient spectroscopy (DLTS) to prove the validity of the simple method. The microstructures and hydrogen bonding configurations of a-Si:H films with different hydrogen dilutions are investigated by using spectroscopic ellipsometry (SE) and Fourier transform infrared spectroscopy (FTIR) respectively. Lower values of interface state density ($D_{it}$) are obtained by using a-Si:H film with more uniform, compact microstructures and fewer bulk defects on crystalline silicon deposited by HWCVD.

**Keywords:** amorphous silicon, microstructure, hydrogen bonding configurations, interface state density

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## 1. Introduction

The heterojunction with intrinsic thin-layer (HIT) solar cell is a kind of high efficiency solar cell with a record cell efficiency of 25.6% (on 143.7 $cm^2$).[1] The heterojunction includes two kinds of semiconductors, of which the simple fabrication method is to deposit the amorphous silicon on a crystalline silicon wafer by plasma-enhanced chemical vapor deposition (PECVD) or HWCVD. The high efficiency of this kind of solar cell originates from high open-circuit voltage acquired by low carrier recombination rate at the interface between the intrinsic amorphous silicon and crystalline silicon.[2] So the amorphous/crystalline interface plays a key role in dominating the behavior of the amorphous/crystalline silicon heterojunction solar cell. The passivation properties of intrinsic hydrogenated amorphous silicon on crystalline silicon have been widely studied. On the one hand, when epitaxial growth is suppressed at the a-Si:H/c-Si interface and there is an abrupt electronic heterojunction, the bulk quality of the a-Si:H film has an obvious influence on the silicon surface passivation properties.[3] On the other hand, the as-deposited interface state density ($D_{it}$) is determined by the local and non equilibrated silicon network structure at the a-Si:H/c-Si interface.[4] Thus, the passivation effect of the sample is a trade-off between the a-Si:H/c-Si interface and the bulk film material quality, and hydrogen dilution during the film deposition plays an additional crucial role in applying hydrogen atoms to passivate the non saturation dangling bonds,[5] therefore the sample can obtain high effective carrier lifetime ($\tau_{eff}$), low surface recombination velocity ($S_{eff}$), and low interface state density ($D_{it}$).

## 2. Experimental method

Layers of 50-nm thick intrinsic hydrogenated amorphous films were deposited by HWCVD with gas mixtures of silane ($SiH_4$) and hydrogen ($H_2$) on 150-μm thick phosphorous-doped CZ silicon wafers with a resistivity of 2.3 Ω·cm. The lack of ion bombardment in HWCVD compared with ion-bombarded standard PECVD is thought to be beneficial to the quality of c-Si surface passivation due to the reduction in the generation of ion impact defects at the a-Si:H/c-Si interface. Prior to the a-Si:H depositions, the silicon wafers were dipped into potassium hydroxide (KOH) solution to remove the saw damage on the wafers and were cleaned in RCA 1 solution consisting of ammonia/hydrogen peroxide/water ($NH_4OH/H_2O_2/H_2O$) at a temperature of 80 °C for 10 min and RCA 2 solution consisting of hydrochloric acid/hydrogen peroxide/water ($HCl/H_2O_2/H_2O$) at a temperature of 80 °C for 10 min, sequentially. After cleaning, silicon wafers were immersed in 1% hydrofluoric acid for 1 min to remove surface native oxide, rinsed in deionized water, then dried with a nitrogen ($N_2$) gun and immediately loaded into the HWCVD system to avoid being oxidized. As to the a-Si:H film depositions, the hot wires were treated with $H_2$ for 5 min. We varied the hydrogen dilutions, where the $SiH_4$ gas flow was fixed at 4 sccm while the $H_2$ gas flow was changed from 5 sccm to 15 sccm. In the deposition progress, the temperature was kept at 200 °C and the pressure was fixed at 1.8 Pa, respectively.

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The symmetric heterostructure of a-Si:H/c-Si/a-Si:H was fabricated to measure the effective carrier lifetime ($\tau_{\rm eff}$) by a Sinton Consulting WCT-120 lifetime tester system. We then analyzed the effective carrier lifetime ($\tau_{\rm eff}$) to calculate the surface recombination velocity ($S_{\rm eff}$) and the interface state density ($D_{\rm it}$). Also the interface state density ($D_{\rm it}$) was measured by DLTS through using Semetrol DLTS characterization systems on an Al/a-Si/c-Si metal–insulator–semiconductor (MIS) structure. The amorphous structure of the thin film was verified by SE performed on a semilab GES5E system, and the result was analyzed by using the Tanc–Lorenz model. The hydrogen bonding configurations in the thin film were characterized by FTIR on a Nicolet IS50 system. The low-stretching mode (LSM) and high-stretching mode (HSM) were assessed from the peaks near 2000 $\rm cm^{-1}$ and 2090 $\rm cm^{-1}$, respectively.

## 3. Results and discussion

Figure 1 shows the variations of measured effective carrier lifetime ($\tau_{\rm eff}$) with hydrogen dilution, where the bulk Auger and radiative recombination of the silicon wafer have been extracted by using the parameterization of Kerr and Cuevas.[6] Figure 1 reveals that with the increase of $H_2$ gas flow, the effective carrier lifetime ($\tau_{\rm eff}$) increases, which predicates that the microstructures and hydrogen bonding configurations at the a-Si:H/c-Si interface and in the bulk a-Si:H thin film can be improved by the $H_2$.

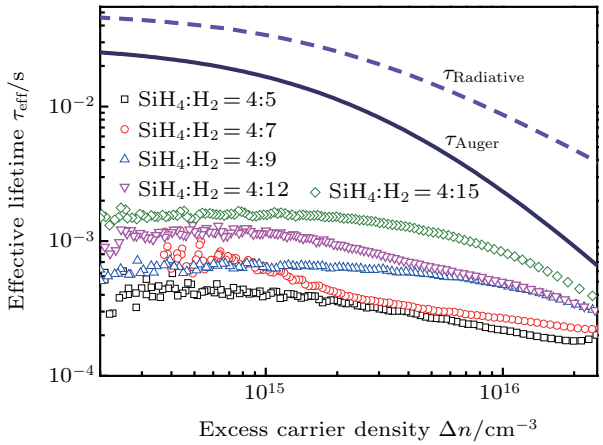



**Fig. 1.** (color online) Variations of measured effective carrier lifetime with hydrogen dilution.

The values of the surface recombination velocity ($S_{\rm eff}$), which can be regarded as a criterion of the passivation quality for a-Si:H film deposited on the silicon surface and can directly be calculated from the measured values of effective carrier lifetime ($\tau_{\rm eff}$) at $\Delta n = 10^{15}$ $\rm cm^{-3}$ according to[7]

$$\frac{1}{\tau_{\rm eff}} = \frac{1}{\tau_{\rm SRH}} + \frac{1}{\tau_{\rm Raditive}} + \frac{1}{\tau_{\rm Auger}} + \left[\frac{W}{2S_{\rm eff}} + \frac{W^2}{D_{\rm n}\pi^2}\right]^{-1},$$

where $W$ is the thickness of the silicon wafer and $D_{\rm n} = 26.9$ $\rm cm^2/s$ is the electron diffusion constant.[8] We ignored the contribution of the Shockley–Read–Hall recombination in silicon wafer to the total recombination since high-quality silicon wafer is used throughout the experiment.

Generally, surface passivation is ascribed to two different mechanisms, namely chemical electronic passivation and field effect passivation. The former is caused by a reduction in defect state density ($D_{\rm it}$) at the a-Si:H/c-Si interface and the latter is due to the formation of a built-in potential to repel the minority charge carriers from the interface.[9,10] Carrier-injection-dependent interface recombination calculations suggest that the passivation mechanism of the a-Si:H/c-Si is chemical surface state passivation originating from Si dangling bond reduction since the dangling bond is saturated by atomic hydrogen, rather than by a field effect.[11] So the band bending is negligible as there is an impractically small surface charge at the surface,[12] and the surface recombination velocity ($S_{\rm eff}$) is related to the interface state density ($D_{\rm it}$) by[13,14]

$$S_{\rm eff} = kT\sigma_{\rm n}\upsilon_{\rm th}D_{\rm it},$$

where $k$ is the Boltzmann constant, $T$ is the temperature in unit Kelvin, $\sigma_{\rm n}$ is the capture cross-section of trap for carrier, and $\upsilon_{\rm th}$ is the carrier thermal velocity. The values of interface state density ($D_{\rm it}$) when $\sigma_{\rm n} = 10^{-16}$ $\rm cm^2$ and $\upsilon_{\rm th} = 10^7$ m/s[15] at room temperature are shown in Table 1.

**Table 1.** Parameters of surface recombination velocity ($S_{\rm eff}$) and interface state density ($D_{\rm it}$).

| Hydrogen dilution | $S_{\rm eff}$/(cm/s) | $D_{\rm it}/10^{11}$ $\rm eV^{-1}{\cdot}cm^{-2}$ |
|---|---|---|
| 4:5 | 17.9 | 6.9 |
| 4:7 | 11.6 | 4.5 |
| 4:9 | 11.1 | 4.0 |
| 4:12 | 6.0 | 2.3 |
| 4:15 | 4.3 | 1.7 |

Figure 2 is the typical DLTS for Al/a-Si/c-Si MIS structure when the $SiH_4$ gas flow is 4 sccm and the $H_2$ gas flow is 7 sccm. Several bias pulses are applied from a depletion bias $V_{\rm R}$ to an accumulation bias $V_{\rm P}$ in order to fill the traps in the Si depletion region. The interface states from bulk traps can be distinguished by analyzing the DLTS amplitude versus the filling pulse height ($|V_{\rm R}–V_{\rm P}|$), because the shape and the maximum position of DLTS signal for the case of interface states both change with filling pulse height while the shape and the maximum position of DLTS signal relating to bulk traps remain unchanged.[16,17] The interface states are inherently point defects and their capture and emission rates are dependent on the occupations of electrons or holes of the defect energy level. The change filling pulse height will affect their capture and emission rates and thus the corresponding peak shapes and maximum positions in DLTS spectrum will change. However, bulk traps have a uniform distribution with negligible dependence of the emission rate, and changing the

filling pulse height will only affect their capture rates, but their emission rates will not be affected, and corresponding peak shape and maximum position in DLTS spectrum will remain unchanged. The maximum position in DLTS spectrum, relating to interface states, appears at about 160 K when pulse height is above 5 V and it is absent at the smaller filling pulse height. The interface state density ($D_{it}$) is given by[18,19]

$$D_{it} = -\frac{\varepsilon_{Si} A C_{acc} N_D \Delta C}{kTC_R^3 \ln(t_2/t_1)},$$

where $\varepsilon_{Si}$ is the permittivity of silicon $\sim 10^{-12}$ F/cm, $A$ is the area of the capacitor, $C_{acc}$ is the accumulation capacitance, $C_R$ is the depletion capacitance, $C$ is the maximum DLTS signal, $N_D$ is the substrate doping concentration, $k$ is the Boltzmann constant, and the sampling time $t_2/t_1 = 10$. The interface state density ($D_{it}$) value can be calculated to be $2.4 \times 10^{11}$ cm$^{-2}$·eV$^{-1}$ at midgap, a value comparable to the result of Simoen *et al.*,[20] they had found the interface state density ($D_{it}$) value to be $1.1 \times 10^{11}$ cm$^{-2}$·eV$^{-1}$ at midgap also by the DLTS method. So both the DLTS method and the simple method in this paper yielded interface state density ($D_{it}$) value of the order of $1 \times 10^{11}$ cm$^{-2}$·eV$^{-1}$ at midgap.

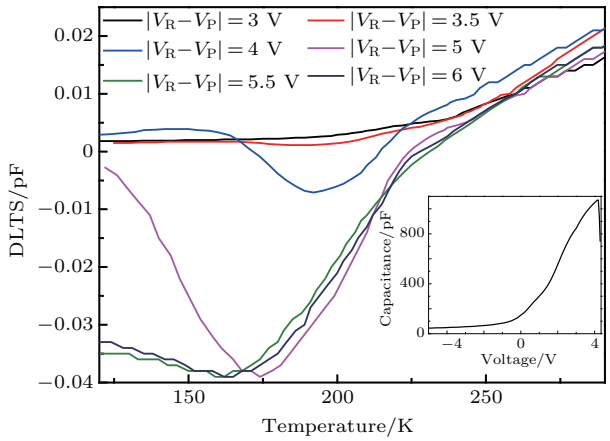



**Fig. 2.** (color online) Variations of DLTS with temperature of Al/a-Si/c-Si MIS structure for n-type Si substrate. The inset shows *C*–*V* characteristics at high frequency for MIS structure.

In order to understand the passivation mechanism in more detail, we used SE and FTIR to characterize the a-Si:H thin film deposited on the c-Si wafer. SE is competent to determine the microstructure of a-Si:H based film by measuring the optical constants, and the Tauc–Lorentz model is usually used to fit the measured data to obtain the imaginary part $\langle\varepsilon_2\rangle$ of the pseudo-dielectric function.[21] Within this approach, $\langle\varepsilon_2\rangle$ is given by the following equations:

$$\varepsilon_2(E) = \begin{cases} \dfrac{AE_0C(E-E_g)^2}{E\left[(E^2-E_0^2)^2+C^2E^2\right]}, & E > E_g, \\ 0, & E \le E_g, \end{cases}$$

where $E_g$ is the optical gap, $A$, $E_0$, and $C$ denote the amplitude, position, broadening of the Tauc–Lorentz oscillator, respectively.

Figure 3 shows the values of imaginary part $\langle\varepsilon_2\rangle$ of a-Si:H thin film with various hydrogen dilutions, extracted from the SE spectra. In general, the biased estimator ($\chi^2$) is used to assess the quality in the fitting of spectroscopic ellipsometry data. The values of the biased estimator ($\chi^2$) are 0.27189, 0.24230, 0.32138, 0.36418, and 1.01101, respectively, which are very small for all samples, indicating very acceptable fits.[22] A characteristic peak near the 3.7 eV indicates that the as-deposited film has an amorphous structure and the growth of the crystalline silicon phase is suppressed.[23] When the hydrogen dilution is increased, the peak in the imaginary part $\langle\varepsilon_2\rangle$ spectrum becomes broader. The higher the amplitude of the imaginary part $\langle\varepsilon_2\rangle$ of the film , the lower the void volume fraction is,[24] which leads to better passivation quality for a-Si:H /c-Si interface.

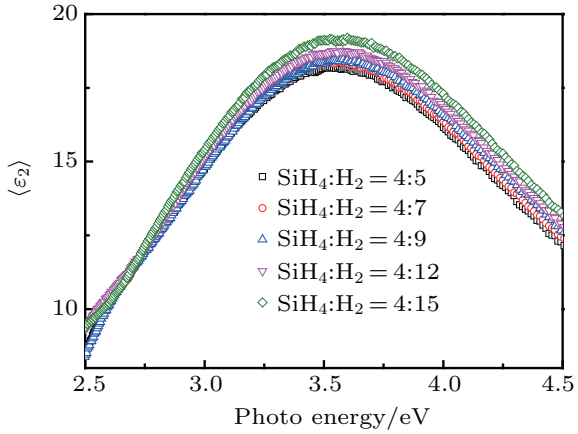



**Fig. 3.** (color online) Distributions of the imaginary part of the pseudo-dielectric function, $\langle\varepsilon_2\rangle$, with different hydrogen dilutions, extracted from the spectroscopic ellipsometry.

Because the a-Si:H/c-Si passivation quality depends significantly on hydrogen bonding configuration in the film, we examine the FTIR spectrum of the a-Si:H film. Due to the fact that the hydrogen bonding configuration close to the interface cannot be detected in the bulk-integrating infrared spectrum, an alternative approach is to measure the a-Si:H bulk properties and use a double-Gasussian-function fitting to analyze the FTIR spectrum.[25]

Figure 4 depicts the variations of the stretching mode with wavenumber at 2000 cm$^{-1}$ related to the LSM which is assigned to the stretching vibration of monohydrides (Si–H) and at 2090 cm$^{-1}$ related to the HSM which is attributed to the vibration of dihydrides (Si–H$_2$) at the internal surfaces of voids, respectively.[26] We can clearly find that LSM and HSM absorption peaks both decrease with the increase of hydrogen dilution as shown in Fig. 4, which is, hypothetically, because of effusion of H$_2$ from the a-Si:H thin film layers.[27] We must bear in mind that there must be abundant hydrogen atoms to passivate the silicon dangling bonds with the increase of hydrogen dilution.

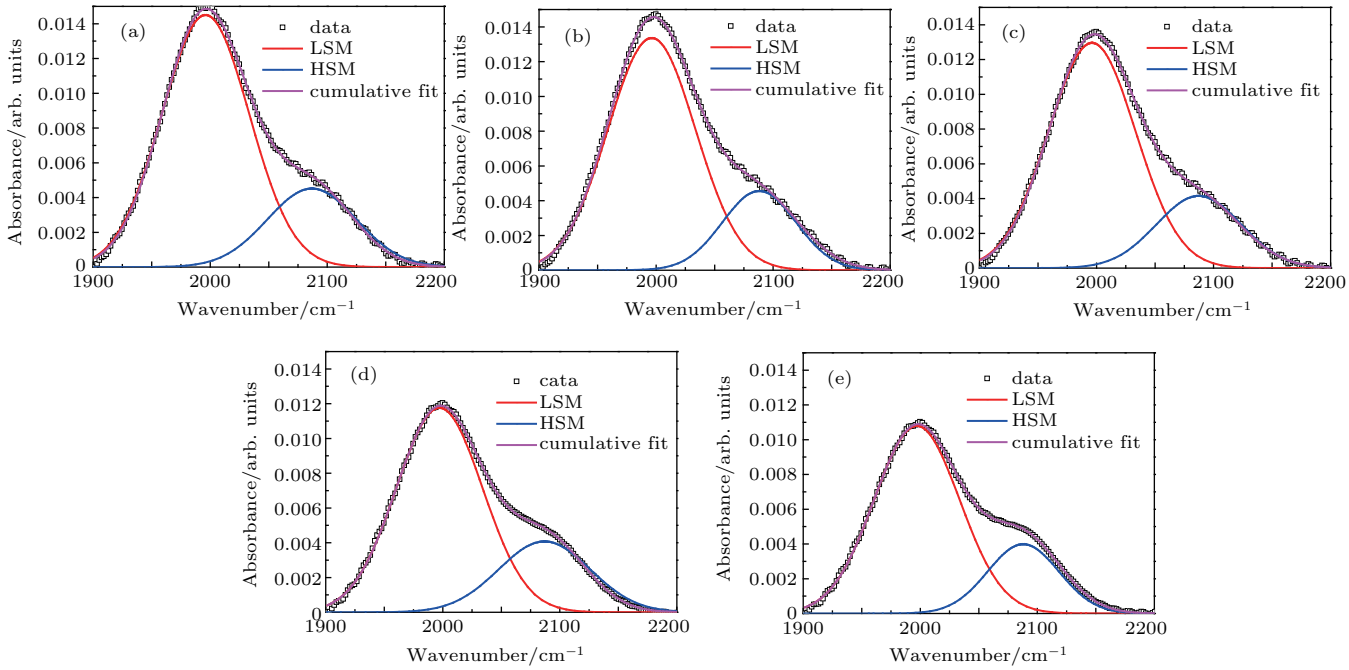



**Fig. 4.** (color online) FTIR spectra of the amorphous silicon films deposited with different hydrogen dilutions in a wavelength range of 1900 cm$^{-1}$–2200 cm$^{-1}$ for (a) $SiH_4$:$H_2$ =4:5, (b) $SiH_4$:$H_2$ =4:7, (c) $SiH_4$:$H_2$ =4:9, (d) $SiH_4$:$H_2$ =4:12, (e) $SiH_4$:$H_2$ =4:15.

It is very well known that an a-Si:H/c-Si interface with a high HSM absorption peak relating to structural defects is harmful to the interface passivation quality,[28] and the voids are related to the low imaginary part $\langle\varepsilon_2\rangle$ of the pseudo-dielectric function as shown in Fig. 3, so the film with both high imaginary part $\langle\varepsilon_2\rangle$ and low HSM is advantageous to the passivation quality for a-Si:H /c-Si interface.

For insufficient hydrogen dilution, there exists excess incorporation of HSM in the as-deposited a-Si:H film. This excess incorporation is the effect of high silane related species in the gas decomposition process.[29] Therefore, the silicon network of the a-Si:H film is richer in voids and structural defects. A void fraction corresponds to an "implied uncovered c-Si surface fraction", and the dangling bonds of the c-Si surface are not saturated.[4] Meanwhile, the bulk defects in the a-Si:H thin film will give rise to the problem of defect-assisted tunneling recombination, thus deteriorating the passivation effect.[30] By promoting the hydrogen dilution, higher hydrogen flux will affect the growing surface, leading to the fact that more weak Si–Si bonds rupture and transform into strong Si–Si bonds.[31] Meanwhile, the surface atoms will acquire more mobility to locate the more energetically stable and orderly bonding sites,[32] so a thin film layer with fewer voids and bulk defects is obtained. Therefore the a-Si:H thin film with more uniform, compact microstructure and fewer bulk defects will cover more c-Si surface fractions. In addition, the hydrogen atoms can move rapidly over the film surface, and into the thin film to saturate the dangling bonds at the interface and in the a-Si:H bulk film, leading to the improvement in the passivation quality.[33] Thus during the hydrogen dilution promotion in intrinsic hydrogenated amorphous silicon deposition processing, the passivation effect will increase the effective carrier lifetime ($\tau_{\rm eff}$), reduce the surface recombination velocity ($S_{\rm eff}$), thereby reducing the interface state density ($D_{\rm it}$).

## 4. Conclusions

In summary, the amorphous/crystalline silicon heterojunction solar cell has high open-circuit voltage and high efficiency due to excellent passivation of the silicon wafer surface by thin intrinsic amorphous silicon layer. Amorphous silicon is deposited on crystalline silicon by HWCVD to analyze the properties of the amorphous/crystalline interface passivation by WCT-120, DLTS, SE, and FTIR. We suggest that the a-Si:H film with more uniform, compact microstructure and fewer bulk defects can cover more c-Si surface fractions during the hydrogen dilution promotion in intrinsic hydrogenated amorphous silicon deposition processing. Meanwhile, the hydrogen atoms can move rapidly on the film surface, and also into the thin film to saturate the dangling bonds at the interface and in the a-Si:H bulk film. Thus, the chemical electronic passivation effect will increase the carrier effective lifetime ($\tau_{\rm eff}$), reduce the surface recombination velocity ($S_{\rm eff}$), thereby decreasing the interface state density ($D_{\rm it}$). Most importantly, a simple method of determining the interface state density ($D_{\rm it}$) derived from lifetime measurement is proposed and its validity is proved by DLTS measurement.

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