# Annealing optimization of hydrogenated amorphous silicon suboxide film for solar cell application

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**Abstract:** We investigate a passivation scheme using hydrogenated amorphous silicon suboxide (a-$SiO_x$:H) film for industrial solar cell application. The a-$SiO_x$:H films were deposited using plasma-enhanced chemical vapor deposition (PECVD) by decomposing nitrous oxide, helium and silane at a substrate temperature of around 250 ℃. An extensive study has been carried out on the effect of thermal annealing on carrier lifetime and surface recombination velocity, which affect the final output of the solar cell. Minority carrier lifetimes for the deposited a-$SiO_x$:H films without and with the thermal annealing on 4 Ω·cm p-type float-zone silicon wafers are 270 $\mu$s and 670 $\mu$s, respectively, correlating to surface recombination velocities of 70 cm/s and 30 cm/s. Optical analysis has revealed a distinct decrease of blue light absorption in the a-$SiO_x$:H films compared to the commonly used intrinsic amorphous silicon passivation used in solar cells. This paper also reports that the low cost and high quality passivation fabrication sequences employed in this study are suitable for industrial processes.

**Key words:** a-$SiO_x$:H; thermal annealing; PECVD

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## 1. Introduction

High-efficiency silicon solar cells feature low surface and bulk recombination rates, which can limit the open circuit voltage and the fill factor of solar cell[1]. Applying an effective surface passivation scheme in order to reduce surface recombination is a precondition for obtaining high efficiency solar cells. This is particularly true for heterojunction solar cells: these cells have an abrupt discontinuity at the interface between the crystalline silicon and the amorphous silicon (a-Si:H) emitter, which leads to a high density of dangling bonds and results in a large density of defects in the bandgap[2]. Passivation schemes commonly used in photovoltaic applications are silicon dioxide ($SiO_2$)[1], silicon nitride ($SiN_x$)[3, 4], hydrogenated intrinsic amorphous silicon (a-Si(i):H)[5] and amorphous silicon carbide[6]. The highest efficiencies reported in the literature have been achieved with $SiO_2$ surface passivation, however, the $SiO_2$ is grown at around 1000 ℃ and not readily applicable to industrial processes due to the issue of high cost. Surface passivation with intrinsic, hydrogenated amorphous silicon (a-Si:H) deposited by plasma-enhanced chemical vapour deposition (PECVD) at around 225 ℃, results in the same low effective surface recombination velocity as thermal oxidation[7]. However, Fujiwara *et al.*[8] stated that the growth of a-Si:H at temperatures > 130 ℃ often leads to an epitaxial layer formation on the c-Si, reducing solar cell performance. Also, due to the inherent strong blue light absorption, only ultrathin a-Si(i):H films can be allowed to prevent losses.

Recently, using hydrogenated amorphous silicon suboxides (a-$SiO_x$:H) as the passivation film was reported[9] and excellent passivation results were demonstrated. However, the high frequency (70 MHz) RF power and the hydrogen gas source used in this study are not suitable for industrial solar cell fabrication.

A large amount of hydrogen atoms are produced in the plasma during the deposition of $SiO_x$:H, which is believed to provide additional bulk defect passivation in the silicon material and, consequently, improves the efficiency of the solar cells. Is not only the plasma that contains a high concentration of hydrogen, so does the amorphous silicon suboxide film itself[10]. Therefore, the $SiO_x$:H film also acts as a source of hydrogen in subsequent post-deposition anneals and provides additional bulk defect passivation[11]. In our report, we use PECVD by decomposition of nitrous oxide, helium and silane at a substrate temperature of around 250 ℃ to deposit hydrogenated amorphous silicon suboxides (a-$SiO_x$:H) and obtain an effective lifetime of 270 $\mu$s on 4 Ω·cm p-type float-zone silicon, and up to 670 $\mu$s after annealing under a nitrogen atmosphere. Additionally, the optical analysis shows much less light absorption compared with a-Si:H(i).

## 2. Experimental

To verify the passivation effectiveness, we have fabricated several samples from two-sided polished (100)-oriented boron-doped float-zone (FZ) wafers with a thickness of 380 $\mu$m and a resistivity of 4 Ω·cm. Firstly, we used the standard RCA cleaning method to clean the entire wafer. After removing any potential native oxides by a 30 s dip in a 5% HF solution, we deposit hydrogenated amorphous silicon suboxides (a-$SiO_x$:H) films with a thickness of about 100 nm on each side the wafer in a 13.56 MHz direct PECVD reactor. The following conditions were used: the $SiH_4$ gas flow is 10 sccm, the gas flow ratio of $SiH_4 : N_2O = 1$, the excitation power is 100 W and the deposition temperature $T_{dep}$ is 250 ℃. The workflow followed can be found in Fig. 2 and the cell design is schematically shown in Fig. 1.

After the deposition, three of the samples were annealed

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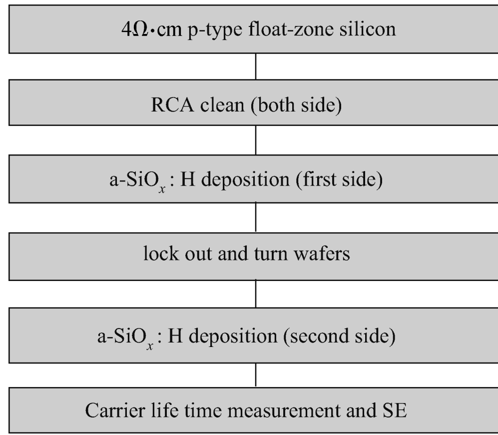


Fig. 1. Workflow of the lifetime investigation.

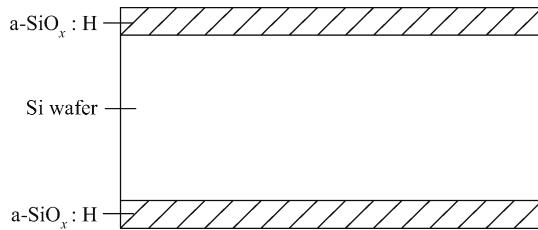


Fig. 2. Structure of the design.

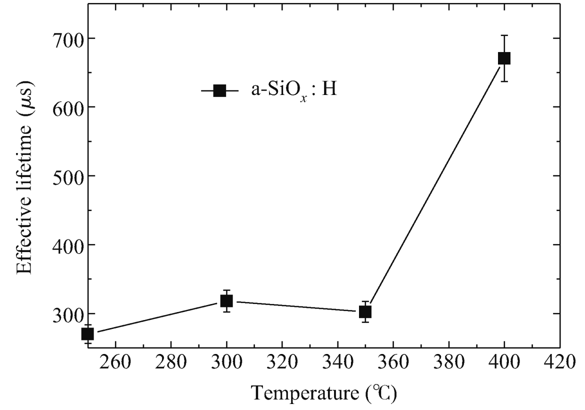


Fig. 3. Measured effective lifetime as a function of the annealing temperature for a-SiO$_x$:H passivated wafers and the sample without annealing for comparison.

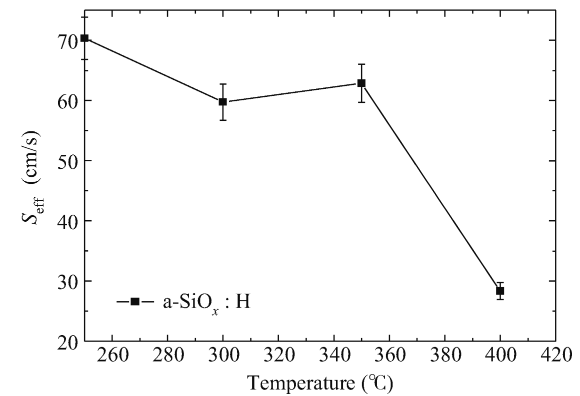


Fig. 4. Calculated surface recombination velocity as a function of the annealing temperature for annealed a-SiO$_x$:H passivated samples.

under a nitrogen atmosphere at 300, 350 and 400 ℃, respectively. Microwave-detected photoconductance decay techniques (MW-PCD) were used to determine the effective carrier lifetime of the samples. The optical characteristics of the hydrogenated amorphous silicon suboxides (a-SiO$_x$:H) films prepared by PECVD are characterized by spectroscopic ellipsometry (SE).

## 3. Results and discussion

To determine the passivation quality of the a-SiO$_x$:H films, the overall recombination of free carriers is evaluated via effective lifetime measurements using the MW-PCD technique. The effective lifetime can be expressed as follows for simplify:

$$1/\tau_{\text{eff}} = 1/\tau_{\text{bulk}} + 1/\tau_{\text{surface}}, \tag{1}$$

where $\tau_{\text{eff}}$ is the measured effective lifetime, $\tau_{\text{bulk}}$ is the bulk lifetime (which combines the Auger, radiative and Shockley-Read-Hall recombinations) and $\tau_{\text{surface}}$ is the characteristic surface recombination lifetime component related to surface recombination through defects and emitter recombination, which is determined by the wafer thickness $W$ and surface recombination $S_{\text{eff}}$. From Eq. (1), it can be concluded that a high $\tau_{\text{eff}}$ indicates a good passivation.

Since the mechanism of passivation imposed by the hydrogenated amorphous silicon suboxides (a-SiO$_x$:H) layer is strongly related to the hydrogen bonds and ions within the film network, metastability effects are expected when high energy photons irradiate this material or when thermal annealing processes are superimposed after PECVD. As reported in Fig. 1 the measured effective lifetime is only 270.14 $\mu$s just after deposition, but it increased quickly when the annealing temperature is higher than 350 ℃ and reaches 670.63 $\mu$s at 400 ℃. An even higher effective lifetime is expected when the annealing temperature is higher than 400 ℃.

We have designed the wafer to be two-sided symmetrical passivated and we can assume that both surfaces provide a sufficiently low recombination velocity and have the same value ($S_{\text{eff}} = S_{\text{front}} = S_{\text{back}}$). The effective surface recombination velocity ($S_{\text{eff}}$) can be expressed by

$$S_{\text{eff}} = W/2 \times (1/\tau_{\text{eff}} - 1/\tau_{\text{bulk}}), \tag{2}$$

where $W$ is the thickness of the wafer. As the bulk lifetime $\tau_{\text{bulk}}$ of float-zone crystal is so large, we use $\tau_{\text{surface}}$ to express $\tau_{\text{eff}}$ approximately and then $S_{\text{eff}}$ can be expressed by

$$S_{\text{eff}} = W/2\tau_{\text{surface}}. \tag{3}$$

However, the value of $S_{\text{eff}}$ that depends on the value of the bulk effective lifetime and the bulk lifetime $\tau_{\text{bulk}}$ of float-zone crystal is so large, that we calculate the upper limit of the surface recombination velocity by omitting the recombinations that occur in the bulk. It implies that the effective surface recombination velocity $S_{\text{eff}}$ is always well below 100 cm/s and would get down to less than 30 cm/s after annealing at 400 ℃ (Fig. 4). However, when the annealing temperature is equal to or less than 350 ℃, there is no obvious improvement. The subsequent annealing of the samples at about 400 ℃ drastically in-

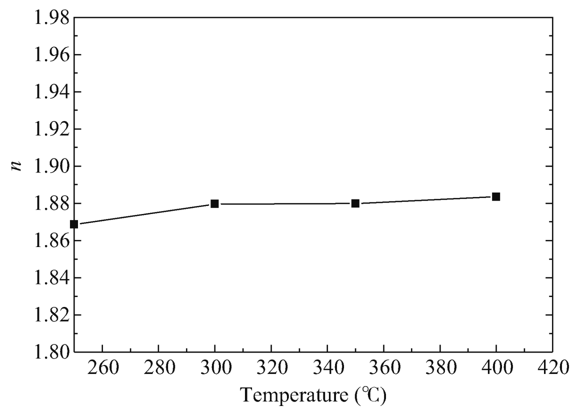


Fig. 5. Refractive index ($n$) of the a-$SiO_x$:H layer as a function of the annealing temperature and the sample without annealing for comparison.

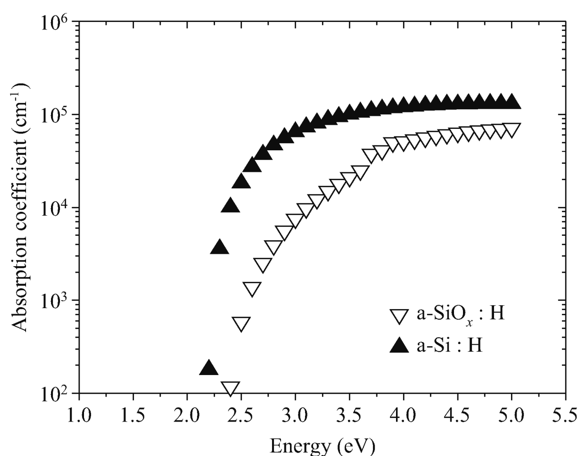


Fig. 6. Absorption coefficient of a-$SiO_x$:H deduced from SE data fitting compared with a-Si:H film.

creases the effective carrier lifetime (Fig. 3). We attribute this increase to the diffusion of hydrogen in the amorphous silicon suboxide layer to the interface and effective passivation of dangling bond states[12]. Figure 5 shows the effect of the annealing temperature on the refractive index of the film. No significant change in the value of refractive index and the thickness of the layer were observed for the samples fired at different temperatures.

In order to learn more about the a-$SiO_x$:H film, we have used spectroscopic ellipsometry (SE) measurements to obtain the optical properties of the a-$SiO_x$:H film. We have the refractive index $n$ and the extinction coefficient $k$, and the absorption coefficient $\alpha$ is calculated by

$$\alpha = \frac{4\pi k}{\lambda}. \quad (4)$$

Figure 6 shows $\alpha$ as a function of the photon energy for a-$SiO_x$:H film compared to that of a-Si:H. The absorption in the a-SiO$x$:H film in the light region above 3.0 eV is significantly lower than that of a-Si(i):H. Therefore, for the same thickness of the film, the fraction of light transferred to the wafer will increase drastically. The passivation quality depends strongly on the thickness of the passivation film[8, 9], so the thickness could be increased to improve quality with decreasing absorption in the passivation layer.

## 4. Conclusion

In conclusion, we have demonstrated that the a-$SiO_x$:H film has the potential to provide excellent surface passivation and that the manufacture process is suitable for industrial use. We have achieved an effective lifetime of about 270 $\mu$s on a 4 Ω·cm p-type float-zone wafer before annealing, and obtained an effective lifetime of up to around 670 $\mu$s after annealing at 400 ℃. The corresponding up limit of effective surface recombination velocity is less than 30 cm/s. However, when the annealing temperature is equal or less than 350 ℃, there is no obvious improvement. Thermal annealing causes little change to the optic properties of a-$SiO_x$:H films. In addition, the a-$SiO_x$:H films exhibit a very low light absorption when the photon energy is higher than 3 eV compared to a-Si(i):H, which is able to have a thicker passivation layer than standard a-Si(i):H and therefore increases passivation quality.


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