Surface Passivation of Crystalline Silicon by Combination of Amorphous Silicon Deposition with High-Pressure H$_2$O Vapor Heat Treatment

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A high minority carrier effective lifetime $\tau_{\text{eff}}$ of crystalline silicon was achieved by hydrogenated amorphous silicon (a-Si:H) films formed by a combination of plasma-enhanced chemical vapor deposition at 150 ℃ with high-pressure H$_2$O vapor heat treatment. $\tau_{\text{eff}}$ was 1.6 x 10$^{-6}$, 3.0 x 10$^{-6}$, and 1.15 x 10$^{-5}$ s for n-type silicon substrates coated with 3-, 10-, and 50-nm-thick a-Si:H films treated with 1.0 x 10$^6$ Pa H$_2$O vapor heat treatment between 180 and 300 ℃ for 1 h. Light-induced passivation enhancement was demonstrated when 620-nm light was illuminated at the 50-nm-thick a-Si:H surface. $\tau_{\text{eff}}$ increased from 8.5 x 10$^{-4}$ to 1.15 x 10$^{-3}$ s probably caused by field effect passivation induced by hole trapping at the SiO$_2$ formed by H$_2$O vapor heat treatment for 1 h. On the other hand, $\tau_{\text{eff}}$ was further increased to 1.2 x 10$^{-3}$ s by 1.0 x 10$^6$ Pa H$_2$O vapor heat treatment at 300 ℃ for 3 h for the sample formed with the 50-nm-thick a-Si:H film. However, no increase in $\tau_{\text{eff}}$ was observed by light illumination at the a-Si:H surface, probably because the SiO$_2$ clusters became stable and had no hole trapping property.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has been widely used to passivate the surface of crystalline silicon. The surface recombination velocity of photo-induced minority carriers is effectively decreased and the minority carrier effective lifetime $\tau_{\text{eff}}$ is increased by the formation of a-Si:H layers by plasma enhanced chemical vapor deposition (PECVD) because of dangling bond termination by hydrogen atoms included in a-Si:H layers at the crystalline silicon surface. a-Si:H passivation has been applied to the fabrication of solar cells with a high conversion efficiency such as hetero junction with intrinsic type (HIT) silicon solar cells. However, we believe that it is not easy to directly form high quality a-Si:H and achieve a low recombination velocity because high energy ions and radicals in plasma can cause serious defects increasing the recombination velocity at the silicon surface. Post annealing will be practical to improve silicon surface passivation with a-Si:H.

In this paper, we report a high $\tau_{\text{eff}}$ of crystalline silicon substrates achieved by a-Si:H films formed by PECVD at 150 ℃ followed by post high-pressure H$_2$O vapor heat treatment, which has been developed to reduce the density of defects at the SiO$_2$/Si interface and grain boundaries of polycrystalline silicon. Moreover, we report a light-induced passivation phenomena. $\tau_{\text{eff}}$ increased by 30% when the a-Si:H surface was illuminated by light.

2. Experimental Procedure

30-Ω cm n-type silicon substrates with a thickness of 520 μm and a crystalline orientation of (100) were chosen. The top and rear surfaces were coated with 100-nm-thick thermally grown SiO$_2$ layers formed at 1100 ℃ in dry oxygen atmosphere. The SiO$_2$ layer at the top surface was then removed using 5% diluted hydrofluoric acid. a-Si:H films with average thicknesses of 3, 10, and 50 nm were deposited on the top surface. The average film thickness was estimated by deposition duration with the deposition rate. a-Si:H films were fabricated by inductively coupled plasma CVD at 150 ℃ using 100% SiH$_4$ gas in pressure of 0.67 Pa and a flow rate of 50 sccm. The deposition rate was 0.8 nm/s.

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cidence with the LED light 2-s pulse. The detection accuracy of the present system in the transmissivity was ±0.1%. The integrated voltage was detected by a digital electrometer and analyzed to obtain \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) using carrier diffusion and annihilation theories.\(^{11,12} \)

### 3. Results and Discussion

The initial n-type silicon samples coated with 100-nm-thick SiO\(_2\) had high \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) about 1.2 \( \times \) 10\(^{-3} \) s. \( \tau_{\text{eff(top)}} \) was the same as \( \tau_{\text{eff(rear)}} \). The silicon surfaces were well passivated by thermally grown SiO\(_2\) layers. If the surface recombination velocities at the top surface \( S_{\text{top}} \) and rear surface \( S_{\text{rear}} \) are independent of light intensity, \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) are given according to carrier diffusion and annihilation theories as\(^{2,13} \)

\[
\begin{align*}
\tau_{\text{eff(top)}} &= \tau_b \sqrt{\frac{D}{\tau_b} \left( 1 - \exp\left(-\frac{d}{\sqrt{D \tau_b}}\right) \right) \left( \frac{D}{\tau_b} + S_{\text{rear}} \right) + \left( \frac{D}{\tau_b} - S_{\text{top}} \right) \exp\left(-\frac{2d}{\sqrt{D \tau_b}}\right)}, \\
\tau_{\text{eff(rear)}} &= \tau_b \sqrt{\frac{D}{\tau_b} \left( 1 - \exp\left(-\frac{d}{\sqrt{D \tau_b}}\right) \right) \left( \frac{D}{\tau_b} + S_{\text{top}} \right) + \left( \frac{D}{\tau_b} - S_{\text{rear}} \right) \exp\left(-\frac{2d}{\sqrt{D \tau_b}}\right)}.
\end{align*}
\]

where \( D \) is the minority carrier diffusion coefficient, \( d \) is the substrate thickness, and \( \tau_b \) is the minority carrier bulk lifetime. A high effective lifetime means a low \( S_{\text{top}} \) and \( S_{\text{rear}} \). If \( \tau_b \) and \( \tau_{\text{eff}} \) are long enough, eqs. (1) and (2) can be simply approximated as

\[
\tau_{\text{eff(top)}} \sim \tau_{\text{eff(rear)}} \sim \frac{d}{S_{\text{top}} + S_{\text{rear}}}. \quad (3)
\]

Equations (1)–(3) indicate that high \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) have almost the same value when \( S_{\text{top}} \) and \( S_{\text{rear}} \) are independent of light intensity. We previously revealed that coincidence between \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) was obtained when the minority carrier diffusion length \((D \tau_{\text{eff}})^{0.5}\) was longer than the thickness of the substrate.\(^{12} \) In the present condition of hole minority carriers, \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) have the same value when they are longer than 4 \( \times \) 10\(^{-4} \) s. \( S_{\text{top}} \) and \( S_{\text{rear}} \) were therefore estimated to be about 22 cm/s for the initial n-type silicon samples.

When SiO\(_2\) layers at the top surface of silicon substrates were removed, \( \tau_{\text{eff(top)}} \) was markedly decreased to about 1.6 \( \times \) 10\(^{-5} \) s from the initial value of 1.5 \( \times \) 10\(^{-3} \) s because the bare surface had a high recombination velocity. \( \tau_{\text{eff(rear)}} \) was also decreased to 1.2 \( \times \) 10\(^{-3} \) s. Photo-induced carriers generated at the rear surfaces diffused toward the top surfaces and annihilated there. \( S_{\text{top}} \) was estimated from \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) to be about 3000 cm/s.

Figure 2 shows \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) as a function of thickness of a-Si films formed at the top surface. Arrows present \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) for samples with as-SiO\(_2\) removed at the top surface. Our deposition conditions should be further improved to achieve complete surface coverage with thin a-Si:H films. On the other hand, \( \tau_{\text{eff(rear)}} \) was hardly changed by a-Si:H film formation. The result of the independence of \( \tau_{\text{eff(rear)}} \) with the thickness of a-Si:H films is strange. An increase in \( \tau_{\text{eff(top)}} \) should be associated with an increase in \( \tau_{\text{eff(rear)}} \) because photo-induced minority carriers diffuse from the top surface to the rear surface when the diffusion length of photo-induced minority carriers is longer than the substrate thickness of 520 \( \mu \)m with \( \tau_b \) above 2.3 \( \times \) 10\(^{-4} \) s. Since the initial \( \tau_{\text{eff(top)}} \) was 1.5 \( \times \) 10\(^{-3} \) s, much higher than 2.3 \( \times \) 10\(^{-4} \) s, photo-induced minority carriers were capable of diffusing from the top surface to the rear surface. We interpret that plasma damage occurred at both surfaces. The top surface would have been passivated by a-Si:H film formation, but simultaneously suffered from plasma damage. The rear surface would have only suffered from plasma damage and \( \tau_{\text{eff(rear)}} \) would be decreased.

Figure 3 shows \( \tau_{\text{eff(top)}} \) and \( \tau_{\text{eff(rear)}} \) as a function of heating temperature of 1 \( \times \) 10\(^{-6} \) Pa H\(_2\)O vapor heat treatment for 1 h for samples with a-Si:H film of 3 (a), 10 (b), and 50
samples coated with 50-nm-thick a-Si films. The experimental results of Fig. 3 revealed that samples coated with 50-nm-thick a-Si:H at the top surface had a \( \tau_{\text{eff}} \) value about 30\% higher than the \( \tau_{\text{eff}} \) value at the rear surface. Although those values were lower than 4 \( \times 10^{-4} \) s, in the cases of 1.0 \( \times 10^4 \)-Pa H\(_2\)O vapor heat treatment at 180 and 220 °C. This result indicates a different physics of passivation from the carrier annihilation story with independent recombination velocities of light intensity as discussed above.

To clarify this phenomenon experimentally, we measured \( \tau_{\text{eff}} \) for the following four different types of light illumination for samples with 50-nm-thick a-Si:H annealed at 180 °C, as shown in Fig. 4. \( \tau_{\text{eff}} \) was measured by light illumination at the top a-Si:H films at an intensity ranging from 0 to 1.5 mW/cm\(^2\) with the top surface in the dark, case I (open circles and solid line) and with a bias light at 0.25 mW/cm\(^2\) illuminated at the rear surface, case II (open squares and solid line). \( \tau_{\text{eff}} \) was also measured by light illumination at the rear SiO\(_2\) films at an intensity ranging from 0 to 1.5 mW/cm\(^2\) with the top surface in the dark, case III (solid circles and dashed line) and with a bias light at 0.25 mW/cm\(^2\) illuminated at the a-Si:H films, case IV (solid squares and dashed line). A high \( \tau_{\text{eff}} \) ranging from 1.1 \( \times 10^{-3} \) to 1.15 \( \times 10^{-3} \) s was observed in the cases of light illumination at the a-Si:H films of cases I, II, and IV. On the other hand, low \( \tau_{\text{eff}} \) ranging from 8.0 \( \times 10^{-4} \) to 8.5 \( \times 10^{-4} \) s were observed in the cases III and II for the top a-Si:H surface in the dark. Those results clearly show that light-illuminated a-Si:H had a role in the improvement of surface passivation and increase in \( \tau_{\text{eff}} \).

Changes in photo-induced carrier density per unit area were measured as a function of time in the case of 50-nm-thick a-Si:H samples with 1.0 \( \times 10^4 \)-Pa H\(_2\)O vapor heat treatment at 180 °C for 1 h, as shown in Fig. 5. The samples were illuminated at the top a-Si:H surface at 1.5 mW/cm\(^2\) for an initial 10 s and continuously illuminated at the rear surface [curve (a)], illuminated at the rear surface at 1.5 mW/cm\(^2\) for initial 10 s and continuously illuminated at the top a-Si:H surface [curve (b)], only continuously illuminated at the top a-Si:H surface at 1.5 mW/cm\(^2\) with
keeping the rear surface dark [curve (c)], and only continuously illuminated at the rear surface at 1.5 mW/cm² with keeping the top surface dark [curve (d)]. The carrier density for curve (a) was the same as that for curve (b) until 10 s. It was also the same as the sum of the carrier densities for curves (c) and (d). It rapidly decreased to the level of curve (c) immediately after light termination at 10 s. It subsequently decreased gradually to that for curve (d). This clearly shows that light-illuminated a-Si:H films maintained good passivation for a long time with a time constant of about 3 s. On the other hand, in the case of curve (b), the carrier density rapidly decreased to that for curve (c) at 10 s and subsequently leveled off. These experimental results of Figs. 4 and 5 clearly indicate that the illumination of a-Si:H has an unique role in improving surface passivation. Although we have unfortunately not established a physical theory to explain this interesting phenomenon yet, we give a possible model on the basis of our experiences.

The measurement of optical absorption revealed that 50-nm-thick a-Si:H films absorbed 3% of the incident 620 nm light. Hole and electron carriers were generated in the a-Si:H films. We believe that hole carriers were trapped in the a-Si:H films, which were annealed with high-pressure H₂O vapor heat treatment. Hole trapping bent the silicon band at the surface region according to the strict charge neutrality rule given by the Euler condition and caused an electron accumulation region at the surface resulting in the decrease in S_eff(top) and in the increase in τ_eff(top). We already confirmed that the density of surface trapped states and plasma damage were decreased by high-pressure H₂O vapor heat treatment. Moreover, oxygen atoms were introduced into the a-Si:H films during high-pressure H₂O vapor heat treatment. Si–O bondings were substantially formed by breaking Si–H bonding. We also reported that unstable SiOₓ played a role in hole trapping states. We interpret that our condition of high-pressure H₂O vapor heat treatment for 1 h formed unstable Si–O bondings trapping hole carriers generated by light illumination, although interface traps and plasma damage must have been reduced. Electron carriers generated by light illumination would be diffused out into crystalline silicon because the a-Si/c-Si structure was conductive. A τ_eff(top) of 1.15 × 10⁻³ s and a τ_eff(rear) of 9.3 × 10⁻⁴ s were obtained for high-pressure H₂O vapor heat treatment at 180 °C. Those τ_eff values resulted the S_eff(top) decreasing from 28 (dark) to 18 cm/s when the a-Si:H film was illuminated by 620-nm light. However, the band structure of the a-Si:H/Si layered structure in a dark field was not clear for samples annealed with high-pressure H₂O vapor for 1 h. a-Si:H and crystalline silicon have very different band gaps. The band offset between the a-Si:H/Si interface has also been precisely investigated. It has been reported that the difference in their conduction band edges can be small, while the difference in their valence band edges can be large. However, our present samples had no metal electrodes and no metal oxide semiconductor structure. τ_eff was measured in a floating condition with no standard potential voltage. We therefore did not have information of the initial band bending at the silicon surface.

From our experiences, high-pressure H₂O vapor heat treatment for a long time and at high temperatures effectively decreased the density of dangling bonds in silicon and at its surface, and the treatment changes unstable SiOₓ (x < 2) to stable SiO₂. We applied 1.0 × 10⁶-Pa H₂O vapor heat treatment for a long time of 3 h. Figure 6 shows τ_eff(top) and τ_eff(rear) as a function of heating temperature of 1 × 10⁶-Pa H₂O vapor heat treatment for 3 h for samples with a-Si:H films of 3 (a), 10 (b), and 50 (c) nm thicknesses formed at the top surfaces. No substantial improvement in τ_eff was observed for samples with 3-nm-thick a-Si:H films, as shown in Fig. 6(a) compared with the case of H₂O vapor heat treatment for 1 h, as shown in Fig. 3(a). Slight increases in τ_eff were observed for samples with 10-nm-thick a-Si:H films for 1 × 10⁶-Pa H₂O vapor heat treatment at 180 and 300 °C. However, τ_eff(top) was still larger than τ_eff(rear) in the cases of high-pressure H₂O vapor heat treatment at 180 and 300 °C, as shown in Fig. 6(b). This indicates that the light-induced passivation was still effective in the case of 3 h H₂O vapor heat treatment. On the other hand, τ_eff(top) and τ_eff(rear) were much increased by 1 × 10⁶-Pa H₂O vapor heat treatment for samples with 50-nm-thick a-Si:H films. In particular, τ_eff(top) was increased to 1.2 × 10⁻³ s and τ_eff(rear) was increased to 1.4 × 10⁻³ s by 1 × 10⁶-Pa H₂O vapor heat treatment at 300 °C for 3 h, as shown in Fig. 6(c). Those τ_eff were close to the initial τ_eff of 1.5 × 10⁻³ s for the initial samples with both surfaces coated with 100-nm-thick thermally grown SiO₂. Both silicon surfaces were well passivated with a combination of a-Si:H film formation with high-pressure H₂O vapor heat treatment at 300 °C.

In the case of 50-nm-thick a-Si:H samples with 1.0 × 10⁶-Pa H₂O vapor heat treatment at 300 °C for 3 h,
3 (a), 10 (b), and 50 (c) nm thicknesses formed at the top surfaces.

Light intensity was 1.5 mW/cm$^2$ annealed at 300 °C for different light illumination modes for samples with 50-nm thick a-Si:H. Our previous study revealed that oxygen incorporation by high-pressure H$_2$O vapor heat treatment for 3 h was small 1 at. % on average at most, and that the optical band gap was hardly changed by the treatment. These findings suggest that SiO$_2$ was formed as small cluster structure in a-Si:H films. Our model is therefore that high-pressure H$_2$O vapor heat treatment for 3 h well passivated the a-Si:H/c-Si interfaces and formed stable SiO$_2$ clusters, which did not trap photo-induced hole carriers, so that no light-induced passivation was observed. Light-induced passivation probably occurred associated with unstable SiO$_x$ bonds trapping hole carriers. Although our model has not been experimentally established, the experimental results of Figs. 3–5 clearly demonstrate interesting light induced passivation in the case of illumination of a-Si:H. Those results stimulate further material investigation of stable species to be incorporated to cause effective light-induced passivation by their photo-induced holes or electrons.

### 4. Conclusions

We investigated the surface passivation of n-type crystalline silicon coated with a-Si:H films at the top surface, which were annealed in 1.0 × 10$^6$ Pa H$_2$O vapor for 1 and 3 h. The 9.35-GHz microwave transmittance measurement system with 620-nm light illumination at the top a-Si:H films as well as the rear SiO$_2$ films was used to measure $\tau_{\text{eff}}$. High $\tau_{\text{eff}}$ values of 1.6 × 10$^{-4}$, 3.0 × 10$^{-4}$, and 1.15 × 10$^{-3}$ s at maximum were achieved by 1.0 × 10$^6$ Pa H$_2$O vapor heat treatment between 180 and 300 °C for 1 h for samples with the top surfaces formed with a-Si:H films with thicknesses of 3, 10, and 50 nm, respectively. Light-induced enhancement in $\tau_{\text{eff}}$ was observed when light was illuminated to the 50-nm-thick a-Si:H films. $\tau_{\text{eff}}$ increased by about 30% when the a-Si:H films were illuminated. The enhancement in $\tau_{\text{eff}}$ was maintained for a long time with a time constant of 3 s, when the light was off. Electrical field effect passivation was probably caused by hole trapping at SiO$_2$ clusters formed in the a-Si:H films by 1.0 × 10$^6$ Pa H$_2$O vapor heat treatment for 1 h. On the other hand, heat treatment at 300 °C with 1.0 × 10$^6$ Pa H$_2$O vapor for 3 h increased $\tau_{\text{eff}}$(top) to $1.2 \times 10^{-3}$ and $\tau_{\text{eff}}$(rear) to $1.4 \times 10^{-3}$ s, which were close to the initial $\tau_{\text{eff}}$ of $1.5 \times 10^{-3}$ s for samples with both surfaces coated with 100-nm-thick thermally grown SiO$_2$. No enhancement in $\tau_{\text{eff}}$ was observed when a-Si:H films were illuminated in that case.

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