Passivation Mechanisms of Atomic Layer-deposited AlO$_x$ Films and AlO$_x$/SiO$_x$ Stack

Lei Gong$^{1,2}$, Chunlan Zhou$^{1,2,*}$, Junjie Zhu, Wenjing Wang$^{1,2}$, Fangxu Ji$^{1,2}$

$^1$The Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, Chinese Academy of Science (CAS), Beijing 100190, PR China
$^2$University of Chinese Academy of Sciences (UCAS), Beijing 100190, PR China
$^3$Solar Energy Department, Institute for Energy Technology, Kjeller, Norway
$^*$E-mail: zhouchl@mail.iee.ac.cn

Abstract. A new passivation layer of AlO$_x$/SiO$_x$ were prepared, in which 80 nm SiO$_x$ was prepared by spin-coating perhydropolysilazane (PHPS) and annealed at 450°C. In order to compare the passivation effect of single AlO$_x$ layers and the SiO$_x$/AlO$_x$ stack on silicon surface, the fixed charge (Q$_f$) in the passivated layers and chemical passivation effect were obtained by corona charge method. Fourier transform infrared spectroscopy (FTIR) and Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to investigate the Si-H, Si-O bonds and the hydrogen profile in the passivation layer, respectively. The result reveals that the single layer of AlO$_x$ provides good field effect with a large amount of negative Q$_f$. Furthermore, SiO$_x$ capping on AlO$_x$ have more excellent chemical passivation because of amount of H saturate the dangling bonds on the silicon surface.

1. Introduction
Dangling bonds are formed on the surface of the silicon due to the broken of periodicity, causing a large increase in carriers surface recombination velocity [1]. Surface passivation technology can effectively reduce the of carriers surface recombination velocity and increase effective minority carrier lifetime $\tau_{\text{eff}}$ of silicon by chemical passivation and field-effect passivation [2, 3]. Chemical passivation reduces the interface state density (D$_{it}$). For example, H and O atoms can saturate the dangling bonds at the silicon surface; the field effect passivation forms electric field which electrostatically shields the charge carriers from the interface, so the carrier surface recombination velocity can be reduced because of the lower possibility of meeting for the two type of carriers. A decreased surface recombination velocity means higher carrier lifetimes and thus higher efficiency cells. Different passivation materials have different fixed charge polarities. Among the commonly used passivation materials, AlO$_x$ has negative fixed charges [4], while SiO$_x$ and SiN$_x$ have positive fixed charges [5]. AlO$_x$ have attracted considerable attention due to their excellent surface passivation properties, surface recombination velocities below 10 cm/s have been demonstrated for several deposition methods of AlO$_x$ layers such as atomic layer deposition (ALD), plasma-enhanced chemical vapor deposition (PECVD), and atmospheric pressure chemical vapor deposition (APCVD) [6-9]. However, in order to improve the firing stability, the Al$_2$O$_3$ layer usually is capped with a PECVD silicon nitride (SiNx) layer [10]. In this work, we used PHPS to fabricate SiO$_x$ capping layer on the ALD AlO$_x$ passivation layers to improve the passivation on silicon surface, and compare the passivation quality of ALD AlO$_x$ and AlO$_x$/SiO$_x$ stacks and their passivation mechanism.
2. Experiments
In the experiment, an N-type double-sided polished c-Si substrate was adopted with resistivity of 1~10 Ω·cm. After immersing in H₂SO₄:H₂O₂=4:1 (volume ratio) for 10 minutes at 85 °C and rinsing in DI water, 1% HF was used to remove the surface oxide layer. The AlOₓ layer with different thicknesses of 5-20 nm was prepared by ALD on both sides of the substrate and was annealed in an air atmosphere at 400 °C for 10 min. The mixed solution of PHPS: n-butyl ether = 1:2 (volume ratio) was spun-coating on the double-side AlOₓ surface at 4500 r/min for 60 s and then the coating was baked at 150 °C for 3 min. Finally, the AlOₓ/SiOₓ stack is annealed in air atmosphere at 450 °C for 15 min. To exclude the effect of annealing step after deposition of SiOₓ layers on AlOₓ, we compare the passivation effect of AlOₓ annealing at 400 °C for 10 min and two-step annealing which is annealing at 400 °C for 10 min and then at 450 °C for 15 min in an air atmosphere, the results show there is little different in the τ_eff. So a single AlOₓ was just annealed in an air atmosphere at 400 °C for 10 min as a reference.

Ellipsometer was used to obtain the thickness of AlOₓ and SiOₓ layers. In this paper, the SiOₓ layer thickness is identical at 80 nm. The lifetime samples were characterized using the Microwave Photoconductive Decay (μ-PCD, WT 2000, Semilab) method and the interface fixed charge was measured by the corona charge method using the same device. The chemical bond of the sample was characterized by FTIR, and the profile of H⁺ and SiH⁻ in passivation layers was tested by TOF-SIMS.

3. Results and Discussions
For samples with different AlOₓ thicknesses, we measured the τ_eff, Q_i and minimum minority lifetime (τ_min) by corona charge method to evaluate the total passivation effect, field-effect passivation effect and chemical passivation effect of the film. Figure 1 shows the function of τ_eff with the corona charge for silicon passivated by single AlOₓ film and the AlOₓ/SiOₓ stack. By continuously applying charges opposite to Q_i to the surface of the sample, the electric field provided by the additional charge is used to offset the effect of field effect passivation, and the τ_eff continues to decrease. As the additional charge increases further until the field effect passivation is completely cancelled, τ_eff reaches a lowest value τ_min. The amount of charge applied at this point is regarded as the amount of Q_i of the interface. The τ_min has a strong positive relationship with the chemistry passivation effect, namely the reverse relationship with D_n. The corona charge decreases to 200 from 250 nC/cm² and τ_min is up to 400 from 300 μs after capping SiOₓ layer on AlOₓ. This means that the Q_i amount declines slightly while D_n has been evidently reduced. As the charge continues to be applied, the excess charge will again provide the effect of field effect passivation, so there will be a corresponding increase in τ_eff. The τ_eff and τ_min of the single layer of AlOₓ and AlOₓ/SiOₓ stacks of different AlOₓ thicknesses are shown in Fig. 2. As the thickness of AlOₓ increases from 5 nm to 20 nm, the τ_eff of both structures is gradually increasing, and the increasing trend is gradually slowing down. In addition, we measured that τ_eff of the single-layer SiOₓ is about 350 μs. Comparing with the single-layer SiOₓ and AlOₓ, the τ_eff of the stack is higher than that of the single passivation layer, which means the passivation effect of the stack is better. The thickness of AlOₓ shows little effect on Q_i of the two structures, the fixed charge of all single-layer AlOₓ samples is maintained at −1.6 × 10¹²/cm², while the fixed charge of the AlOₓ/SiOₓ stack is −1.3 × 10¹²/cm². This means that the SiOₓ cap will slightly weaken the field passivation while increasing the chemical passivation. It also indicates regardless of in the single AlOₓ or in the stack, that the main reason for the improvement of the passivation effect as the thickness of AlOₓ increases is the enhancement of chemical passivation.
Figure 1. The corona charge curve of 15 nm AlO$_x$ and the AlO$_x$/SiO$_x$ stack. The corona charge and $\tau_{\text{eff}}$ at the lowest point represents the field-effect passivation and the chemical passivation, respectively.

Figure 2. $\tau_{\text{eff}}$ and $\tau_{\text{min}}$ of single layer of AlO$_x$ and the AlO$_x$/SiO$_x$ stack varies with the thickness of AlO$_x$ layer. The AlO$_x$ layer was annealed in atmosphere at 400°C for 10 min. After that, SiO$_x$ was prepared and the stack was annealed in atmosphere at 450°C for 15 min.

In order to investigate the difference in the chemical passivation effect of these three structures, FTIR was measured and the results are shown in Fig. 3(a). After thermal treatment, PHPS has basically been converted into SiO$_x$, a small amount of Si-N is remained but it is negligible compared with Si-O. The Si-H peak at 2200 cm$^{-1}$ of AlO$_x$ and the AlO$_x$/SiO$_x$ stack plays a major role on chemical passivation. The absence of Si-H bonds in the single-layer SiO$_x$ film illustrates the limited passivation effect ($\tau_{\text{eff}} = 350$ μs) because of the poor chemical passivation. Figure 3(b) presents the results of TOF-SIMS for the stack. It shows that the concentration of H$^+$ is at a high level in both SiO$_x$ layer and AlO$_x$ layer. We can find an obvious peak of SiH$^+$ near the surface of the Si substrate, which means an amount of H combined with Si to form Si-H and saturate the dangling bonds on the silicon surface. The result of FTIR indicates that there is no Si-H peak in the single layer of SiO$_x$. However,
SiH$^+$ in the SiO$_x$ layer of the AlO$_x$/SiO$_x$ stack is obvious. This may due to H in the AlO$_x$ which diffuses into the layer and is stored in it by combining with Si atoms.

![FTIR and TOF-SIMS results](image)

**Figure 3.** FTIR and the TOF-SIMS results. (a) is the FTIR spectrum of SiO$_x$ layer, AlO$_x$/SiO$_x$ stack and AlO$_x$ layer; (b) is the TOF-SIMS spectrum of AlO$_x$/SiO$_x$ stack. The position of each layer is marked in the figure. The sputter area is a square of 5 μm * 5 μm.

4. Conclusions

In this paper, we present a new stack passivation layers of ALD AlO$_x$/SiO$_x$, in which 80 nm SiO$_x$ was prepared by coating a PHPS precursor and annealed at 450°C in air atmosphere. If using single SiO$_x$ layer to passivate the Si surface, the $\tau_{\text{eff}}$ is about 340 μs because it just provides the field-effect passivation. However, as for the single layer of AlO$_x$, $\tau_{\text{eff}}$ increases from 700 μs to 890 μs while thickness of AlO$_x$ increasing from 5 nm to 20 nm. The negative fixed charge keeps constant but the chemical passivation increase with the increase of AlO$_x$ thickness. After capping on AlO$_x$ with SiO$_x$, the surface passivation of Si improves further, and $\tau_{\text{eff}}$ is in the range of 820-1150 μs as AlO$_x$ thickness varies from 5 nm to 20 nm. Even though $Q_f$ decreases from $-1.6\times10^{12}$cm$^2$ to $-1.3\times10^{12}$cm$^2$ after
capping SiO$_x$ layers, the amount of H saturate the dangling bonds on the silicon surface still improves the surface passivation of Si.

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6. References
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