

Performance and Light Stability of Electron-Selective TiO₂ with an AlO_x Interlayer

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Abstract

We have investigated effects of different tunnel oxide layers on the performance and light stability of tunnel oxide/TiO₂ stack electron-selective contacts on *n*-type Si. From the study, we found that although chemical SiO₂ and thermal atomic layer deposited AlO_x tunnel layers show higher passivation performance, plasma-enhanced atomic layer deposited AlO_x tunnel layers demonstrate light-enhanced τ_{eff} with an ITO capping layer as well as the highest light stability without an ITO capping layer. Meanwhile, the results of X-ray photoelectron spectroscopy analysis demonstrate that ultrathin AlO_x tunnel layers result in no change in the band alignment between TiO₂/*n*-Si, compared to SiO₂ interlayers.

1. Introduction

Recently, carrier-selective contacts (CSCs) for crystalline silicon (c-Si) photovoltaics (PV) have attract a tremendous amount of interest in academic and industrial photovoltaic research areas. In this concept, a set of dopant-free carrier-selective contacts (CSCs) is employed to separate and collect photogenerated free carriers in a cell structure [1]. Up to now carrier-selective contact materials such as metal oxides, fluorides, and organic polymers have been studied and significant progress has been made [2]-[9]. Among the electron-selective transport materials described above, TiO₂ is one of the few industrially matured materials and various fabrication techniques have been developed to deposit TiO₂ thin layers.

Meanwhile, it was reported that the band alignment of a TiO₂ thin layers with a Si substrate is clearly affected by the presence of an interlayer between a TiO₂ thin layer and a Si substrate [10]. In addition, it has been widely known that similar to ALD AlO_x passivation layers, the passivation performance of ALD TiO₂ layers can be largely enhanced under light illumination due to a light-enhanced negative fixed charge density in TiO₂ passivation layers [11]. However, the light stability of ultrathin electron-selective TiO₂ contacts has not been evaluated.

Therefore, in this study, we have investigated effects of different tunnel oxide layers on the performance and light stability of the fabricated tunnel oxide/TiO₂ stack electron-selective contacts for developing high-performance light-stable electron-selective contacts.

2. Experimental Details

Double-side shiny-polished *n*-type Fz Si wafers ((100)-orientation, resistivity of 1-5 $\Omega \cdot \text{cm}$, thickness of 285 μm)

were used to fabricate tunnel oxide/TiO₂ stack-based electron-selective contact passivated samples. After wafer cleaning with the standard RCA procedure, ultrathin chemical SiO₂ tunnel layers with about 1.2 nm thickness and ultrathin plasma-enhanced ALD (PEALD) and thermal ALD (TALD) AlO_x tunnel layers with sub-1 nm thickness were fabricated on the cleaned and HF-lasted Si wafers. Finally, ~3.5-nm-thick TALD TiO₂ electron-selective transport layers were deposited on the tunnel oxide passivated Si wafers. After the deposition, all fabricated samples experienced forming gas annealing (FGA).

Effective minority carrier lifetime (τ_{eff}) of the symmetrically passivated samples was obtained by QSSPC measurements with a Sinton WCT-120 photoconductance lifetime tester at high injection levels. The thickness and chemical composition of the prepared layers and their interface with a Si wafer were determined from ellipsometry measurement and X-ray photoelectron spectroscopy (XPS) measurement of single-side passivated samples, respectively.

For investigating light stability of the symmetrically passivated samples with/without ~100-nm-thick indium tin oxide (ITO) capping layers fabricated by remote plasma deposition (RPD) technique, we measured time-dependent changes of τ_{eff} of the prepared samples under AM1.5G illumination at 1-sun intensity and 25 \pm 1 $^{\circ}\text{C}$ (STC) after a certain time interval.

3. Results and Discussion

Fig. 1 shows the Si 2*p* peaks of SiO₂ interlayers in the fabricated samples. The fitted Si 2*p* peaks show that the formation of Si-O-Ti and Si-O-Al bonds as well as the formation of a thinner and lower quality SiO_x interlayer in the sample with a TALD AlO_x tunnel layer compared to the sample with chemical SiO₂ and PEALD AlO_x tunnel layers. Formation of a thinner and lower quality SiO_x interlayer under an ultrathin TALD AlO_x layer seems to be due to a small number of deposition cycles and weak oxidizing power of H₂O for a TALD process. From the results, we could conclude that chemical composition and thickness of SiO_x interlayers seem to be significantly affected by stack materials and/or fabrication processes of tunnel oxide layers.

We investigated performance and light stability of the fabricated samples under AM1.5G illumination at 1-sun intensity and 25 \pm 1 $^{\circ}\text{C}$, respectively. After FGA processes the samples with PEALD AlO_x tunnel layers demonstrate inferior passivation quality to other samples, and the samples with chemical SiO₂ tunnel layers show the highest level of passivation quality among the samples, and J_0 of ~12 fA/cm²,

implied open-circuit voltage iV_{oc} of ~ 689 mV, and implied fill factor iFF of ~ 81 % could be obtained from the samples with chemical SiO_2 tunnel layers (data not shown here).

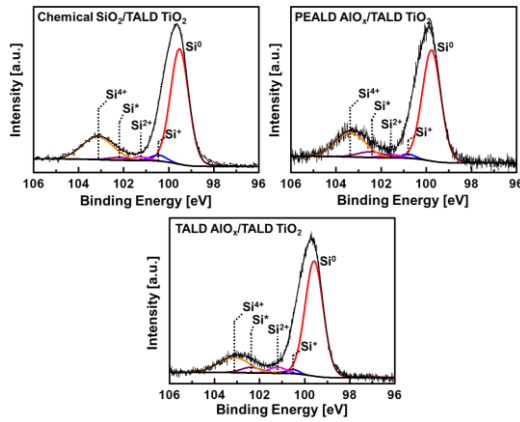


Fig. 1 Fitted XPS spectra of Si 2p peaks measured from the samples with chemical SiO_2 (top-left), PEALD AlO_x (top-right), and TALD AlO_x (bottom) tunnel layers, respectively. Si $2p_{1/2}$ peaks of Si^0 peaks have not shown for simplicity. Si^* peaks show the presence of Si-O-Ti bonds (top-left) and Si-O-Al bonds (top-right and bottom).

However, as shown in Fig. 2, the samples with PEALD AlO_x tunnel layers show the highest light stability (e.g., degradation of $\tau_{eff} < 20$ %) compared to other samples (e.g., degradation of $\tau_{eff} > 40$ %) after 8000 min of illumination. Meanwhile, the samples with a chemical SiO_2 tunnel layer and a TALD AlO_x tunnel layer show similar degradation behavior. Such inferior light stability seems to be due to low UV-stability of an ultrathin SiO_2 tunnel layer under a thin TiO_2 layer and an ultrathin lower-quality SiO_x interlayer under a TALD AlO_x layer with low film density, compared to a PEALD AlO_x layer with high film density. Meanwhile, ~ 100 -nm-thick ITO capping layers seem to enhance light stability of all ultrathin tunnel oxide/ TiO_2 stack-passivated samples though surface damage of the ultrathin tunnel oxide/ TiO_2 stack-passivated samples during an ITO deposition process cannot be fully recovered by FGA. In addition, although light-enhanced τ_{eff} of ultrathin tunnel oxide/ TiO_2 stack-passivated samples cannot be observed for all samples without an ITO capping layer, light-enhanced τ_{eff} can be observed from PEALD AlO_x tunnel oxide/ TiO_2 stack-passivated samples only. However, the enhanced τ_{eff} also decreases eventually.

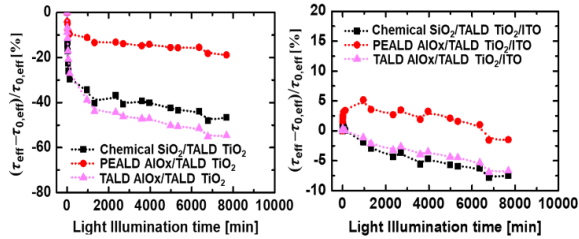


Fig. 2 Time evolution of the effective minority carrier lifetime τ_{eff} of the fabricated samples under AM1.5G illumination at 1-sun intensity and 25 ± 1 °C without (left) and with (right) ~ 100 -nm-thick ITO capping layers.

Finally, we deduced the band alignment of the samples using by XPS and UV-Vis-NIR spectroscopy according to Kraut's method (data not shown here) [10]. Chem. SiO_2 and ALD AlO_x tunnel oxide layers show no difference of band alignment and this could be due to the very low fixed charge density in ultrathin ALD AlO_x tunnel oxide layers and/or the surface Fermi level strongly pinned by (plasma) damage on c-Si surfaces during ALD AlO_x deposition processes. Higher light stability of PEALD AlO_x tunnel oxide layers seems to be due to the high mass density and/or low hydrogen content of PEALD AlO_x tunnel layers, which effectively protect Si/ SiO_x interfaces from light illumination. From the results, we could conclude that ultrathin sub-1nm-thick PEALD AlO_x tunnel oxide layers could enhance light stability of TiO_2 electron-selective contacts without a change of band alignment, compared to Chem. SiO_2 tunnel layers.

3. Conclusions

The passivation performance and light stability of electron-selective TiO_2 contacts on n -type c-Si substrates with different ultrathin tunnel oxide interlayers have been investigated. Ultrathin tunnel oxide/ TiO_2 stack electron-selective contacts show significant light instability. However, ~ 100 -nm-thick ITO capping layers could largely reduce light instability of the TiO_2 electron-selective contacts. In addition, ultrathin sub-1-nm-thick PEALD AlO_x tunnel layers could provide enhanced light stability of TiO_2 electron-selective contacts without a significant change of band alignment compared to Chem. SiO_2 and TALD AlO_x tunnel layers.

Acknowledgements

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References

- [1] J. Melskens, B. W. H. van de Loo, B. Macco, L. E. Black, S. Smit, and W. M. M. Kessels, IEEE J. Photovolt. **18** (2018) 373.
- [2] S. Avasthi, W. McClain, G. Man, A. Kahn, J. Schwartz, and J. Sturm, Appl. Phys. Lett. **102** (2013) 203901.
- [3] J. Bullock et al., Proceedings of 43rd IEEE Photovoltaic Specialists Conference (2016) 210.
- [4] J. Bullock, M. Hettick, J. Geissbühler, A. J. Ong, T. Allen, C. M. Sutter-Fella, T. Chen, H. Ota, E. W. Schaler, S. De Wolf, C. Ballif, A. Cuevas, and A. Javey, Nat. Energy **1** (2016) 15031.
- [5] Y. Wan, C. Samundsett, J. Bullock, T. Allen, M. Hettick, D. Yan, P. Zheng, X. Zhang, J. Cui, J. McKeon, A. Javey, and A. Cuevas, ACS Appl. Mater. Interfaces **8** (2016) 14671.
- [6] G. Masmitjà, P. Ortega, J. Puigdollers, L. G. Gerling, I. Martín, C. Voz, and R. Alcubilla, J. Mater. Chem. A, **3** (2018) 3977.
- [7] W. Wu, W. Lin, J. Bao, Z. Liu, B. Liu, K. Qiu, Y. Chen, and H. Shen, RSC Adv. **7** (2017) 23851.
- [8] W. Lin, W. Wu, J. Bao, Z. Liu, K. Qiu, L. Cai, Z. Yao, Y. Deng, Z. Liang, and H. Shen, Mater. Res. Bull. **103** (2018) 77.
- [9] H. Imran, T. M. Abdolkader, and N. Z. Butt, IEEE Trans. Electron Devices **63** (2016) 3584.
- [10] M. Perego, G. Seguini, G. Scarel, M. Fanciulli, and F. Wallrapp, J. Appl. Phys. **103** (2008) 043509.
- [11] A. F. Thomson and K. R. McIntosh, Prog. Photovolt: Res. Appl. **20** (2012) 343.