Investigation of atomic-layer-deposited TiO\textsubscript{x} as selective electron and hole contacts to crystalline silicon

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Abstract

The applicability of atomic-layer-deposited titanium oxide (TiO\textsubscript{x}) thin films for the formation of carrier selective contacts to crystalline silicon (c-Si) is investigated. While relatively good electron selectivity was presented recently by other groups, we show that carrier selectivity can be engineered from electron to hole selective depending on the deposition conditions, post deposition annealing and the contact material covering the TiO\textsubscript{x} layer. For both the electron and hole contacts, an open-circuit voltage (V\textsubscript{oc}) of \~{}650 mV is obtained. The fact that the V\textsubscript{oc} is correlated with the (asymmetric) induced c-Si band bending suggests that carrier selectivity is mainly governed by the effective work function and/or the fixed charge rather than by the asymmetric band offsets at the Si/TiO\textsubscript{x} interface, which provides important insight into the basic function of metal-oxide-based contact systems.

Keywords: Titanium oxide; atomic layer deposition; crystalline silicon; solar cell; carrier selective contact

1. Introduction

Carrier selective contact that extracts one type of carrier (electron or hole) out of the light-absorbing material is a subject of current interest for photovoltaic application [1]. In particular, novel carrier selective contacts for crystalline silicon (c-Si) can be used to replace the conventional p-n homojunction and hydrogenated amorphous silicon base [5]. The origin of the electron selectivity of TiO\textsubscript{x} has been ascribed to the asymmetric current flow at the interface, which provides important insight into the basic function of metal-oxide-based contact systems.
silicon (a-Si:H)/c-Si heterojunction schemes for achieving high efficiency without complex device processing. While various high-work-function transition-metal-oxides such as MoOx, WOx, and V2Ox have been demonstrated as hole selective contacts for c-Si solar cells [2-4], efficient electron selective contact has been lacking. Recently, TiOx (or TiO2) thin-layers deposited by atomic layer deposition (ALD) [5] or chemical vapor deposition [6,7] have been reported to act as electron selective contacts to crystalline silicon solar cells. Yang et al. demonstrated a 21.6% efficient solar cell by applying a thermal-ALD TiOx to full-area rear electron contact for N-type monocrystalline silicon base [5]. The origin of the electron selectivity of TiOx has been ascribed to the asymmetric current flow at the Si/TiOx interface where the low conduction band offset allows the electron flow while the high valence band offset hinders the hole flow [5-7]. Meanwhile, it is suggested that ALD-TiOx contain negative fixed charge [8,9], which might be detrimental in aiming for an ideal electron selective contact. In this work, we have investigated the carrier selectivity of TiOx prepared by ALD with different oxidation processes using oxygen plasma and thermal reaction with H2O vapor. Our results show that the carrier selectivity of TiOx is widely tunable from electron-selective ($V_{oc}$$\sim$680 mV) to hole-selective ($V_{oc}$$\sim$650 mV) by the ALD process, post-deposition treatments and contact material that covers TiOx layer.

2. Experiment

We fabricated solar cell precursors as shown in Fig. 1. Si wafers (N-type float zone silicon, 1 Ωcm, (100) orientation, 200 μm thick, planar surface) were RCA-cleaned and HF-dipped prior to deposition process. TiOx was deposited by an ALD system (FlexAL, Oxford Instruments) on the rear-side of c-Si wafer. Titanium isopropoxide (TTIP) was used as a Ti precursor. The oxidation during every ALD cycle took place using either O2 plasma or thermal reaction with H2O vapor. We term these processes as plasma- and thermal-ALD, respectively. Although a substantially longer purge time was required after H2O dose (30 s) than after O2 plasma (2 s), TiOx were deposited at a similar growth rate per cycle of ~0.045 nm in both ALD processes. In this study, to focus on the carrier selectivity of TiOx, an intrinsic a-Si:H buffer layer (8-15 nm) was deposited by plasma-enhanced chemical vapor deposition prior to TiOx. This buffer layer preserves the surface passivation quality unchanged regardless of the ALD condition, as confirmed by measuring the quasi-steady-state photoconductance (QSSPC) [10] before and after TiOx deposition. As a rear contact after ALD-TiOx, four different conductive materials (Ti, Al, Pd, and ITO) were examined. The front-side emitter or front-surface-field (FSF) was formed using a standard heterojunction structure (a-Si:H i-p or i-n stack), following a sputtered ITO layer [4]. As shown in Fig. 1, TiOx acts either as electron contact and back-surface-field (BSF) or hole contact and rear-emitter for N-type base. Suns-$V_{oc}$ measurement [11] was carried out before and after hotplate annealing at 180°C for 15 min in ambient air. Apart from solar cell precursors, TiOx layers were directly

![Fig. 1. Schematic illustration of sample structures studied in this work.](image-url)
deposited on N- and P-type c-Si (1 Ωcm) to measure the induced c-Si band bending by using a surface photovoltage (SPV) technique with a 905-nm laser pulse [12,13].

3. Results and discussion

In Fig. 2, (a) the suns-V_{oc} curves (initial state only) and (b) the corresponding external 1-sun V_{oc} as a figure of merit of the carrier selectivity (both initial and annealed states) are depicted for the two different solar cell precursors shown in Fig. 1. A 6-nm-thick TiO_x layer was deposited on an intrinsic a-Si:H buffer layer either by plasma-ALD (red) or thermal-ALD (blue). For comparison, the results of the standard heterojunction solar cells, i.e., p+NiN and nNiP, are included. In this series, Ti was used as a rear electrode. Note that the positive V_{oc} in Fig. 2 (b) represents the magnitude of electron selectivity (TiO_x and a-Si:H n-layer as electron contacts) while the negative V_{oc} represents the hole selectivity (TiO_x and a-Si:H p-layer as hole contacts). As mentioned earlier, the intrinsic a-Si:H buffer layer between c-Si and TiO_x layer preserves excellent surface passivation, providing an implied V_{oc} at 1 sun illumination of about 720 mV after both plasma- and thermal-ALD TiO_x depositions. It can be seen in Fig. 2(b) that the V_{oc} for the doped a-Si:H references are very close to the implied V_{oc} (iV_{oc}), as expected for a contact featuring good selectivity [14]. Nevertheless, as shown in Figs. 2 (a) and (b), a pronounced variation in carrier selectivity is found for TiO_x contacts depending on the ALD process. It is observed that plasma-ALD TiO_x (red) exhibits electron selectivity rather than hole selectivity. On the other hand, thermal-ALD TiO_x (blue) exhibits rather hole selectivity. In fact, when using a thermal-ALD TiO_x as an electron contact, a negative slope in the suns-V_{oc} curve, i.e., decreasing voltage with

(a)

![Graph](image_url)

(b)

![Graph](image_url)

Fig. 2. (a) suns-V_{oc} curves (initial) and (b) external 1-sun V_{oc} in the initial (ini.) and after annealing (ann.) for different solar cell structures shown in Fig. 1. A 6-nm-thick TiO_x layer was deposited by either plasma- (red) or thermal-ALD (blue). The results of the standard heterojunction solar cells (white) are also shown for comparison. In (b), the positive and negative external V_{oc} represent the magnitude of electron and hole selectively, respectively.
increasing illumination intensity as shown in Fig. 2(a), is observed. This negative ideal factor (n<0) at low illuminations indicates the presence of a non-ideal contact characteristics with respect to extraction of the excess electrons from the absorber [14,15] by the a-Si:H(i)/TiOx/Ti contact. As will be shown in the following by SPV measurements, this poor selectivity is closely linked to the induced c-Si band bending. Furthermore, it is seen in Fig. 2(b) that the post-deposition annealing declines the electron selectivity whereas it enhances the hole selectivity, except for the device with thermal-ALD TiOx used as electron contact. Although the mechanism behind this phenomenon is not well understood, we found that the impact of post-deposition annealing was the strongest when annealing the samples after TiOx/capping layer (Ti, Al, Pd and ITO) stack compared to annealing before metallization (or TCO deposition). This suggests that some chemical reaction takes place at the TiOx/capping layer interface, influencing the carrier selectivity. According to the paper by Yang et al. [5], a reduction reaction of the TiOx layer is occurred by the covering Al layer during annealing due to the stronger oxygen affinity of Al. However, they observed improved electron selectivity by post-deposition annealing, which is clearly opposite from our observation.

To gain insight into the origin of the different carrier selectivity of TiOx, we measured SPV for the plasma- and thermal-ALD TiOx deposited on c-Si (N and P base) without a-Si:H(i) buffer layer. Figure 3(a) shows the induced c-Si band bending (Φ) measured by SPV for these samples before and after annealing. For comparison, the measured Φ for n- and p-type a-Si:H layers (~10 nm) deposited on c-Si are included. These doped a-Si:H contacts demonstrate an ideal band bending (>800 mV) when depositing them on c-Si base with asymmetric polarity, i.e., n on P and p on N. It is evident that plasma- and thermal-ALD induce the band bending in an opposite way, i.e., plasma-ALD TiOx induces greater band bending for P-base than for N-base while the thermal-ALD TiOx induces strong band bending (>800 mV) only for N-base. By plotting external Voc of solar cell precursors versus induced band bending measured by SPV, a correlation is found as shown in Fig. 3(b), indicating that the higher induced-band bending leads to the more efficient carrier selectivity.

![Graph showing SPV signals (Φ) for TiOx layers deposited on p- (top) and n-type (bottom) c-Si in the initial (ini.) and annealed (ann.) states. TiOx was deposited by plasma- (red) or thermal-ALD (blue). For comparison, SPV signals for a-Si:H n and p layers are also shown. (b) Voc of piNi-X (X represents plasma/thermal-ALD TiOx or p/n a-Si:H) and niNi-X samples plotted versus Φ measured on P/X and N/X contacts, respectively. Open and closed symbols represent the initial and annealed states, respectively.](image-url)
Further investigations revealed that the carrier selectivity of TiO$_x$ is significantly influenced by the capping contact material. Figure 4 shows the 1-sun external $V_{oc}$ for solar cell precursors with various contact materials (Ti, Al, ITO, Pd). In Fig. 4, to compare the maximum $V_{oc}$ obtained from each solar cell structure, the $V_{oc}$ of initial state are shown for plasma-ALD TiO$_x$ used as an electron contact while those of annealed state are shown for thermal-ALD TiO$_x$ used as a hole contact. As shown in Fig. 4, among four materials examined in this study, plasma-ALD TiO$_x$ provides the highest electron selectivity when coating it with Al but the lowest one with Pd. An almost inverse behaviour is observed for the hole selectivity of the thermal-ALD TiO$_x$. By combining TiO$_x$ with the best contact material, almost symmetric carrier selectivity from electron selective ($V_{oc}$~ 680 mV) to hole selective ($V_{oc}$~650 mV) is obtained using the plasma-ALD TiO$_x$/Al stack and the thermal-ALD TiO$_x$/ITO stack, respectively. These results indicate that the c-Si band bending is influenced by the work function (WF) of the contact material, as WF of Al is the lowest but that of Pd is the highest among the materials investigated (Ti: 4.3 eV, Al: 4.2 eV, Pd: 5.4 eV [16], ITO: 4.8 eV [17]). Similarly, Allen et al. reported that the deposition of Ca as a low WF metal (<3 eV) on ALD-TiO$_x$ led to an improved electron contact [18]. Based on these results, it is likely that the carrier density in TiO$_x$ is too low so that the screening length of TiO$_x$ layer is well above its thickness. An exception is found for thermal-ALD TiO$_x$/Pd stack, as it shows lower $V_{oc}$ (~580 mV) than that with ITO (~650 mV). Since this TiO$_x$/Pd stack resulted in the highest initial $V_{oc}$ (~630 mV, not shown in the figure), post-deposition annealing of TiO$_x$/Pd stack might degrade the contact properties.

Our results revealed that TiO$_x$ can act as either electron or hole selective contact depending on ALD process and its selectivity is strongly influenced by the post-deposition annealing and WF of metal or TCO contact on top of TiO$_x$ layer. Although the mechanism behind these findings is not yet understood, the band offset at Si/metal-oxide contact does not fully account for the observed carrier selectivity because our thermal-ALD TiO$_x$ acts as hole selective contact despite of the presumed presence of large valence band offset at the Si/TiO$_x$ interface. Rather than this, we propose

![Fig. 4. Influence of capping material (Ti, Al, Pd and ITO) on top of TiO$_x$ layer on external 1-sun $V_{oc}$ of two solar cell precursors with plasma-ALD TiO$_x$ as electron contact (top, initial state) and thermal-ALD TiO$_x$ as hole contact (bottom, annealed state).]
that an asymmetric band bending in c-Si induced by the difference of effective WF and/or fixed charge of metal-oxide contact gives more qualitative explanation for the observed carrier selectivity. Furthermore, we highlight that the need for a capping layer featuring a proper work function limits the applicability of TiO$_x$ in practical contact systems, as high efficiency device requires not only good electrical contact but also proper optical design that often includes low-$n$ transparent conductive oxide layer to minimize the optical absorption loss at the contact.

4. Conclusions

Although the carrier selectivity of our TiO$_x$ is still behind the level of the doped a-Si:H, our results show that it is widely tunable from electron to hole contacts and can be further optimized by the choice of contact material. It can be considered that carrier selectivity of TiO$_x$ is changed by the electrical properties of TiO$_x$, e.g., Fermi level / WF and fixed charge density. To give a more holistic view on the basic function of metal-oxide-based contact systems, the mechanism behind the tunable carrier selectivity of TiO$_x$ and some design rules, simulation results and structural investigations comparing the hole and electron selective TiO$_x$ films will be presented in the future. Further study is also ongoing to improve the carrier selectivity to the level of the doped a-Si:H layers.

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