Full paper

Activating and optimizing evaporation-processed magnesium oxide passivating contact for silicon solar cells

Jing Yu¹,c, Mingdun Lia⁰a, Di Yanb, Yimao Wanga, Hao Lin⁰a, Zilei Wang⁰a, Pingqi Gaod,e, Yuheng Zenga, Baojie Yanb, Jichun Ye¹,*

¹ Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences (CAS), Ningbo City, 315201, PR China
² Research School of Engineering, The Australian National University, Canberra, ACT, 2601, Australia
³ University of Chinese Academy of Sciences, Beijing City, 100049, PR China
⁴ School of Materials, Sun Yat-sen University, Guangzhou, 510275, China

Keywords:
- Passivating contacts
- Dopant-free
- Carrier-selective contacts
- Heterojunction silicon solar cells
- Magnesium oxide (MgOx)

A B S T R A C T

Irrespective of the success on reduction of contact resistivity, lack of chemical passivation of evaporated metal oxides heavily hinders their applications as passivating contacts, such contacts can be an alternative route for high efficiency and cost effective silicon solar cells. Here, we demonstrate that electron beam evaporated magnesium oxide (MgOx) thin film can work as a promising electron-selective passivating contact for n-Si solar cells after a post-annealing treatment and an alumina-initiated atomic hydrogenation. 10 nm MgOx on n-Si provided a surface recombination velocity down to 14.9 cm/s while 1 nm MgOx showed a low contact resistivity of 14 mΩ cm². Comprehensive characterizations revealed the formation of Si–O–Mg bonds and the activation of atomic hydrogens were the main reasons for such high-level passivation. A PERC-like dopant-free rear contact was formed by using the 1 nm-MgOx as electron-collector and the 10 nm-MgOx as passivating layer, the resultant solar cells achieved 27% increment in efficiency and 51 mV increase in open-circuit voltage in comparison with reference devices. The ways of improving passivation quality of MgOx, and novel design of contact structure open up the possibility of using evaporation-processed metal oxides as effective and low-cost carrier-selective passivating contacts for n-Si photovoltaic devices.

1. Introduction

Carrier-selective contacts, which extract only one type of carriers from silicon while blocking the other, are the main topic in the photovoltaic (PV) research community [1–4]. Exploring and lubricating well-developed highly performing contacts to c-Si have become important research directions, especially for high performance electron-selective contacts (ESCs) [5,6]. Recently, various materials working as ESCs for the n-Si solar cells have been explored, including organic polymers [7], alkali metal compounds [8–10], low work function metals [11], metal oxides (e.g., titanium oxide [12], magnesium oxide [13,14], zinc oxide [15,16], tantalum oxide [17]), carbonates [18] and their combinations [19].

In practice, it is challenging to achieve both a good passivation and a low contact resistivity for n-Si wafers by introducing those low work function electron-selective materials, the major reason is the high dependence of passivating qualities (interface properties) on deposition processes [6]. Taking one of the most successful ESCs of TiOx as an example, wide variations in passivation qualities have been reported of depositing TiOx layer on Si wafer using atomic layer deposition (ALD) [12,20], chemical vapor deposition (CVD) [21], sputtering deposition [22] and solution process [23,24]. Yang et al. reported surface recombination velocity (SRV) in the range of 11–56 cm/s for ALD-grown TiOx films between 2.5 and 5.5 nm [12]. For thicker TiOx, the SRV has been reported to be below 1 cm/s [25]. Schwartz et al. fabricated a thin passivating TiOx interface by CVD which resulted in a 16 cm/s SRV value [21]. Meanwhile, a low-temperature solution synthesized TiOx only gave an effective minority carrier lifetime (τ) of 60 μs, which is equivalent to a SRV of 250 cm/s [23]. Sputter-deposition of TiO2 passivation layer decreased the SRV value from 717 to 79.8 cm/s over porous silicon treated multi-crystalline silicon [22]. By now, as we can see only ALD-grown and CVD-coated TiOx layer can well passivate the Si surface. For the evaporated process (physical vapor deposition), metal oxides and their combinations show the similar problem of...
producing insufficient reduction of surface recombination mostly because of the low adhesion and the poor conformal coverage \([6,26]\). Due to the drawback of using evaporation processes, it is still essential to provide an additional interfacial passivation layer, such as a-Si:H and SiO\(_2\), to form carrier-selective passivating contacts for silicon solar cells \([3,17]\).

Among those explored metal oxides, MgO\(_x\) stands out as a good candidate for intensive study due to its easy-of-processing, which can be easily prepared via electron beam evaporation, thermal evaporation, sputtering and solution method \([13]\). It also has nontoxic property, advantageous optical property (3–7.8 eV bandgap) \([27]\) and ideal band alignment when in contact with n-Si. Typically, inserting 1 nm MgO\(_x\) film between the n-Si and aluminum electrode can assist electron transporting from silicon to the electrode. Recently, n-Si solar cells with a full-area thermally evaporated MgO\(_x\) contact at the rear and boron-diffused p\(^+\) emitter with Al\(_2\)O\(_3\)/Si\(_3\)N\(_4\) passivation layer at the front have reached an efficiency up to 20.0\%. However, the contact was not highly competitive due to the low passivation quality fabricated by the evaporated approach. This kind of low passivation contact limits the efficiency of the silicon solar cell, especially results in a low open-circuit voltage \((V_{oc})\) \([14]\).

Herein, we demonstrate effective passivation over c-Si substrates by electron beam deposited MgO\(_x\) followed by a low-temperature post-annealing (at 200 °C in air) and an alumina-initiated atomic hydrogen passivation. As a result, these post treatments can reduce the SRV down to 14.9 cm/s for n-type c-Si wafers (8 Ω cm). Comprehensive characterizations revealed the formation of Si–O–Mg bonds and the activation of atomic hydrogen passivation were the main reasons for such high-level passivation. Moreover, a PERC-like dopant-free rear contact with 1 nm-MgO\(_x\) as electron-transporting layer and 10 nm-MgO\(_x\) as passivating layer was presented to underscore the great potential of MgO\(_x\) for high efficiency silicon solar cells. Dopant-free hybrid solar cells with front n-Si/PEDOT:PSS emitter were used as a platform to examine the effectiveness of rear-sided ESC designs. An efficiency of 15.5\% with \(V_{oc}\) of 623 mV was obtained for the devices featuring PERC-like MgO\(_x\) rear contact, which is 27\% higher in efficiency and 51 mV increase in open-circuit voltage in comparison with reference devices (with the n-Si/Al contact). The ways of improving the passivation quality of MgO\(_x\) as well as the novel contact structure by using the MgO\(_x\) represent the possibility of using evaporated metal oxides as low-cost passivating contacts for high efficiency silicon solar cells.

2. Results and discussion

To investigate the passivation quality of the MgO\(_x\) as an electron-selective passivating contact, double sides polished n-Si wafers (Cz, 5–10 Ω cm) with MgO\(_x\) capping layers on both surfaces were used. The minority carrier lifetime was measured by both a microwave photoconductivity decay system (WT-2000 mPCD, Semilab) and a Sinton WCT-120 lifetime tester which can also extract the \(V_{oc}\) at one sun from the injection-dependent carrier lifetime \(\tau\) \((\Delta n)\). Since the same silicon substrates were used, the measured minority carrier lifetime characterization was performed to compare the passivation effects of MgO\(_x\) contacts \([13]\). Fig. 1 shows the impacts of post-annealing, film thickness and metallization on the passivation quality of MgO\(_x\) thin films. Fig. 1a shows the \(\tau\) at an injection level of 10\(^{15}\) cm\(^{-3}\) of the 10 nm MgO\(_x\) film, as a function of annealing temperatures. As increasing the temperature of post-annealing, the \(\tau\) increased dramatically and reached a maximum value of about 580 μs at an annealing temperature of 200 °C. Further increasing temperature resulted in a sharp drop in the carrier lifetime. Besides, the samples showed the trend of improved passivation quality when extending the post annealing time at a lower temperature below 200 °C (see Fig. S1). This is mainly due to the change of the interfacial states, which will be further discussed below. Effective minority carrier lifetime versus MgO\(_x\) film thickness is indicated in Fig. 1b. One can see that the \(\tau\) increased quickly as increasing the thickness from 0.8 to 10 nm for both as-deposited (from 6.5 to 160 μs) and post-annealed MgO\(_x\) films (from 15 to 580 μs) and then kept nearly constant at a thickness of around 10 nm. This trend may be caused by the configuration changes of the deposited MgO\(_x\) from discrete islands to a continuous thin film \([28]\). In the meantime, the lifetime of post-annealed samples at 200 °C were always much higher than that of the as-deposited samples with the same thickness. The occurrence of a thin interfacial SiO\(_x\) layer and the formation of interface bonds might be the reasons for the high passivation quality.

Except for post-annealing, it was also found that coating the MgO\(_x\) with a thermally evaporated Al thin layer was favored for promotion in the passivation quality of n-Si/MgO\(_x\) as shown in Fig. 1c and d. Based on the good passivation presented by the post-annealed MgO\(_x\) films over n-Si, metallization with Al provided an extra gain for their passivation quality. \(\tau\) of 680 μs and \(V_{oc}\) of 645 mV were achieved after a 5 nm single-side Al film deposition. The surface passivation quality was then remarkably enhanced when both sides were coated with Al layers. As a result, it improved \(\tau\) from 160 to 900 μs, SRV from 1800 to 14.9 cm/s and \(V_{oc}\) from 610 to 660 mV, correspondingly. The boost passivation effect is likely attributed to (i) the low work function of MgO\(_x\)/Al (ii) alumina-initiated atomic hydrogen passivation, which will be discussed below. Generally, when an Al capping layer is deposited on the most passivation layers or electron selective layers, no improvement for the effective lifetime could be found due to the high work function of Al metal \([29,30]\). This further demonstrates the importance of MgO\(_x\) interlayer. Furthermore, the boost passivation effect provides the foundation of fabricating solar cells featuring PERC-like MgO\(_x\) rear contact and indicates the application prospect of the process.

Ag/PEDOT:PSS/textured n-Si heterojunction solar cells (HSCs) with MgO\(_x\)/Al as rear contacts have been fabricated to demonstrate the effectiveness of using MgO\(_x\) layers as ESCs. Fig. 2a presents the structure of the HSCs and Fig. 2b displays the current density-voltage (\(J\)-\(V\)) curves for illuminated HSCs. The results are summarized in Table 1. The series resistance \((R_s)\) was estimated by the slope of the J-V curve. The power conversion efficiency \((\%\) C) of the reference sample (Si/Al) was 12.2\%, with a poor \(V_{oc}\) of 572 mV, short circuit current density \((J_{sc})\) of 30.2 mA/cm\(^2\) and fill factor \((FF)\) of 70.8\%. After inserting 1 nm as-deposited MgO\(_x\) layer, the \(C\) was improved to 13.7\%, with enhanced PV parameters of \(V_{oc}\) (585 mV), \(J_{sc}\) (31.8 mA/cm\(^2\)) and \(FF\) (73.8\%) due to the decreased contact resistivity induced by low work function MgO\(_x\). Interestingly, after a 10 min post-annealing of MgO\(_x\) layer in air (before metallization), further improved rear contact helped to obtain a remarkable \% C of 14.5\% with a promising \(V_{oc}\) of 603 mV and \(J_{sc}\) of 32.5 mA/cm\(^2\) which indicated around 31 mV and 2.3 mA/cm\(^2\) improvement on their \(V_{oc}\) and \(J_{sc}\) values by comparing with the reference cell. The significantly improved \(V_{oc}\) value may be attributed to the improved interfacial MgO\(_x\)/Si states, the formation of Si–O–Mg bonds and the electrostatic potential of the bonds simultaneously reduce charge recombination and leakage current.

To evaluate the electrical behavior of the MgO\(_x\) electron selective contacts, the Cox-Strack method was used for measuring contact resistivity \([31]\). For a clear comparison, the current-voltage (\(I\)-\(V\)) curves for the samples with the rear contacts of n-Si/Al, n-Si/ass-deposited MgO\(_x\) (1 nm)/Al, n-Si/post-annealed MgO\(_x\) (1 nm)/Al, and n-Si/post-annealed MgO\(_x\) (10 nm)/Al, which were collected from the same electrode diameter (1.2 mm), are shown in Fig. 3a. It is evident that the n-Si/Al (without MgO\(_x\) interlayer) exhibited typical Schottky behavior due to the Fermi-level pinning effect caused by the large density of the metal-induced gap stated (MIGS) and unpassivated defects between Al and the Si substrate \([32]\). With the presence of 1 nm as-deposited MgO\(_x\), the contact property changed from the Schottky to an ohmic behavior with a final contact resistivity of 15 mΩ cm\(^2\). The low work function MgO\(_x\) interlayer can alleviate the Fermi level pinning effect and reduce the energy barrier for electrons. The post-annealed 1 nm MgO\(_x\) can further enhance the transportation of the electrons from silicon, due to the improved interfacial states. These results on contact resistivity were
consistent with the results of silicon solar cells with these contacts as shown in Fig. 2b and Table 1. The Si/Al contact had the largest energy barrier for electron transporting at rear side, so the reference cells possessed the worst device performance, while the lowest contact resistivity stemmed from the 1 nm annealed MgOx/Al sample (14 mΩ cm²) resulted into the best device performance in the three kinds of devices. It was worthy noted that the enhancements of solar efficiency were mainly due to the improved interfacial states. Because of the lower boost of passivating effect for both the as-deposited (6.5 μs of minority carrier lifetime) and post-annealed (15 μs of minority carrier lifetime) 1 nm MgOx (as shown in Fig. 1b), we assume that the electrostatic potential of Si–O–Mg bonds are beneficial to the transmissions of electrons from Si to Mg, which furtherly decreased the interface barrier. Moreover, the contact resistivity value of 10 nm MgOx was found to increase dramatically to 3500 mΩ cm², which result in an unacceptable series resistance in the silicon solar cells [33]. Detailed I–V curves of different thicknesses of MgOx interlayer/Al structures are shown in Fig. S2.

As shown above, the 10 nm-MgOx offered excellent passivation (with a SRV down to 14.9 cm/s) with poor contact resistivity, while the 1 nm MgOx showed an excellent contact propert (with a ρc down to 14 mΩ cm²) with unsatisfied passivation quality over the n-Si wafer. Thus, a PERC-like dopant-free rear contact configuration with the 1 nm MgOx as the electron-selective layer and 10 nm MgOx as a passivating layer was straightforwardly presented to underscore the great potential, as schematically shown in Fig. 3b. Since the evaporation is a low-temperature process, such contact structure can be easily fabricated by hard mask patterning. This leads to an extensive simplification and a low cost in terms of the fabrication process. The schematic structure of mask is shown in Fig. S3. The results of silicon solar cells with different area ratios of 1 nm MgOx over 10 nm MgOx are plotted in Fig. 3c and Fig. S4 and summarized in Table 2. In comparison with the full-area 1 nm MgOx contact (100% area ratio), the PERC-like cells with 50% area ratio showed remarkable improvements, Voc was improved from 603 to 623 mV, Jsc was improved from 32.5 to 33.8 mA/cm² and PCE was improved from 14.5% to 15.5%. It can be seen that the improvement in PCE was primarily attributed to the improvement in Voc and Jsc, which manifests the holes blocking effect of MgOx as well as its passivation effects of the thicker MgOx layer. The cells featuring full-area contact of 10 nm MgOx (0% area ratio) exhibit a very low PCE of 1.6%, along with Voc, Jsc, and FF values of 612 mV, 8.9 mA/cm², and 29.3%, respectively. For the PERC-like rear contact, Voc and Jsc depend positively on rear passivation and dc (the distance between rear selective contact), while negatively on the contact fraction. While FF react in

![Fig. 1.](image1)

**Fig. 1.** a) Effective minority carrier lifetime (τ) of the 10 nm MgOx thin-film as a function of annealing temperature. b) Effective minority carrier lifetime versus MgOx film thickness. c) Dependences of lifetime and SRV of the MgOx thin films on different treatments. d) Voc-implanted for samples with different treatments.

![Fig. 2.](image2)

**Fig. 2.** a) Schematic of the Ag-grid/PEDOT:PSS/textured n-Si/MgOx/Al device. b) Light J–V characterization of the solar cells with as-deposited MgOx, post-annealed MgOx and without MgOx interlayer.
The photovoltaic parameters of the PEDOT:PSS/Si-based solar cells without MgOx, with as-deposited MgOx and post-annealed MgOx interlayer.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$V_{oc}$ (V)$^a$</th>
<th>$J_{sc}$ (mA/cm$^2$)$^a$</th>
<th>$FF$ (%)$^a$</th>
<th>PCE (%)$^a$</th>
<th>$Rs$ (Ω cm$^2$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>0.572 (0.570 ± 0.002)</td>
<td>30.2 (30 ± 0.2)</td>
<td>70.8 (70.3 ± 0.5)</td>
<td>12.2 (12.0 ± 0.2)</td>
<td>3.69 (3.79 ± 0.1)</td>
</tr>
<tr>
<td>With 1 nm as-deposited MgOx</td>
<td>0.585 (0.581 ± 0.004)</td>
<td>31.8 (31.5 ± 0.3)</td>
<td>73.8 (73.3 ± 0.5)</td>
<td>13.7 (13.35 ± 0.35)</td>
<td>3.02 (3.22 ± 0.2)</td>
</tr>
<tr>
<td>With 1 nm annealed MgOx</td>
<td>0.605 (0.602 ± 0.003)</td>
<td>32.5 (32.4 ± 0.1)</td>
<td>74.2 (74.0 ± 0.2)</td>
<td>14.5 (14.35 ± 0.15)</td>
<td>2.78 (2.90 ± 0.12)</td>
</tr>
</tbody>
</table>

$^a$ Data and statistics based on five cells of each condition. $^b$ Numbers in bold are the champion values of each condition.

opposite trends to the $d_c$ and in same trends to contact fraction and rear passivation. As the area ratios of 1 nm MgOx film decreased from 100% to 50%, the $d_c$ increased while contact fraction and rear passivation decreased, which decrease $FF$ a bit and increase the $V_{oc}$ and $J_{sc}$ a lot. Consequently, the cell efficiency increased gradually. Further decrease in area ratios of 1 nm MgOx film will lead to large contact resistance due to the bad effects of $d_c$ increase and contact fraction and finally deteriorated $FF$ and $J_{sc}$ and thus the cell efficiency [34,35]. Their external quantum efficiency ($EQE$) spectra were also measured to further show the carrier collection efficiency in a range of wavelength from 300 to 1200 nm, as shown in Fig. 3d. An improvement in $EQE$ was observed for the 1 nm post-annealed MgOx devices compared with the reference samples. As to the 50% area-ratio PERC cells, an additional increment was found in the long wavelength range, which is correlated with the $J_{sc}$ enhancement as indicated in Table 2. Performing post-annealing and inserting a 10 nm MgOx passivation layer to increase the passivation quality were clearly observed in their $EQE$ response.

Routinely improving the contact properties firstly by reducing contact resistivity and then by enhancing passivation leads to increased $V_{oc}$ step by step, with 572, 585, 605 and 623 mV for the contacts of n-Si/Al, n-Si/as-deposited MgOx (1 nm)/Al, n-Si/post-annealed MgOx (1 nm)/Al and n-Si/PERC-like MgOx/Al, respectively. Ultimately the PERC type solar cell showed an efficiency of 15.5%, with significant enhancements on the $V_{oc}$, $J_{sc}$ and $FF$. As a result, 27% efficiency enhancement was achieved on reference solar cells with an efficiency of 12.2%. Compared with conventional n-PERC, the MgOx based PERC-like design can be easily fabricated by hard mask patterning without complex and high-temperature process. The passivation and electron selective dual function can be achieved by the same material. From a carrier-selectivity perspective, when the $\rho_c$ of ESCs decreases to around 10 mΩ cm$^2$ scale, the influence of small $\rho_c$ variation on solar cell efficiency featured a full-rear area contact is negligible. However, confining the contact fraction and increasing $d_c$ play a negative influence on electrons transportation and a positive influence on holes transportation. While the passivation effects of rear side play the opposite influence on carriers. The relative impact that these parameters have on the carrier-selectivity should be traded off. Further optimization on process and area ratio should be completed [1]. Besides, that the efficiency of the silicon solar cells as presented here was limited by the front-sided PEDOT:PSS structure due to the parasitic absorption of PEDOT:PSS layers, poor anti-reflection and inferior coating quality upon the textures [36]. Nevertheless, the silicon solar cells can be further improved in near future by replacing the front hole transport layer of PEDOT:PSS with other more effective functional materials, such as MoOx, VOx etc.

Although we have already achieved excellent passivation properties from the evaporated MgOx and successfully demonstrated its applications as passivating contacts, it is important to investigate the interfacial structural changes to explain the passivation mechanisms. Hence, comprehensive characterizations including X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and secondary ion mass spectroscopy (SIMS) analysis were used to study the interface between silicon substrate and MgOx. The Si 2p XPS spectra of different samples are shown in Fig. 4a. The Si 2p spectra can be divided into three bands: the peak intensity at lower binding energy (99.8 eV and 100.4 eV) attributes to crystalline silicon substrate, the peak intensity at the higher binding energy (~103.2 eV) attributes to Si–O–Si bonds and the other peak intensity in a red curve at medium binding energy (100.8 eV) with a range of from 99.5 to 101.5 eV associates with Si–O–Mg chemical bonds from the mixture of various amorphous magnesium silicates (by synthetically considering the FTIR and SIMS results below) [37]. It is difficult to accurately divide the Si–O–Mg broad band into different components in the light of the complexity and uncertain binding energy from various amorphous magnesium silicates.
However, it is interesting to note that the intensity of Si–O–Mg bond (over other peaks) increased as increasing post-annealing temperature from 25 °C to 200 °C. This indicates that a large amount of amorphous magnesium silicates were formed at the interface between silicon and MgOx. At a higher temperature of 300 °C, the Si–O–Mg bond was broken and leaded a high intensity of SiOx peak. This matches well to the trend of passivation effects refer to Fig. 1a. We assume that the H atoms chemisorbs to different cites at higher temperature, which leads to the nearby Mg–O bond breaking due to the negative charge transfer to a nearby Mg cation during chemisorption [40]. In addition to the impact of Si–O–Mg bond on the passivation quality, we also notice that Si–O–Mg bonds are responsible for the transport of electrons from Si to Mg where Si and Mg are bonded with O, and have charge of 0.342 e and 1.42–1.76 e correspondingly [41,42]. As a result, Si–O–Mg bonds can significantly improve the electronic transmission.

In order to further reveal the roles of chemical bonds on the passivation, the FTIR spectra of the MgOx samples is indicated in Fig. 4c. According to the previous Ref [37], a peak at around 980 cm−1 appeared compared with the as-deposited MgOx film, indicating the linkage between the Si and MgOx. Then, a red shift occurred upon further increasing the temperature to 300 °C, indicating that the Si–O–Mg bonds were changed to Si–O–Si bonds.

In addition to the interfacial characterization, the influence of bulk MgOx film on the passivation effect was further examined by SIMS characterizations shown in Fig. 4b. From Fig. 4b, the existence of SiOx−, SiOH− and MgOH− signal was clearly observed. It was obvious that outer surface (near-surface) film regions contained a large amount of Mg(OH)2, which is consistent with previous results [28,43]. Before and after annealing, the intensity of MgO− signal didn’t change much while the concentration of MgOH− was increased at elevated temperature. This is due to the fact that H+ is easy to be absorbed around the O1s atom [44]. The work function and UV-VIS were also measured.

### Table 2
The photovoltaic parameters of the PEDOT:PSS/Si-based solar cells with different area ratios of 1 nm selective contact MgOx to 10 nm passivation contact MgOx.

<table>
<thead>
<tr>
<th>Area ratio of 1 nm MgOx</th>
<th>(V_{oc} (V))</th>
<th>(J_{sc} (mA/cm^2))</th>
<th>(FF (%))</th>
<th>(PCE (%))</th>
<th>(Rs (\Omega cm^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>0.605 (0.602 ± 0.003)</td>
<td>32.5 (32.4 ± 0.1)</td>
<td>74.2 (74.0 ± 0.2)</td>
<td>14.5 (14.35 ± 0.15)</td>
<td>2.78 (2.90 ± 0.12)</td>
</tr>
<tr>
<td>75%</td>
<td>0.611 (0.610 ± 0.001)</td>
<td>33.0 (32.8 ± 0.2)</td>
<td>73.9 (73.5 ± 0.4)</td>
<td>14.8 (14.65 ± 0.15)</td>
<td>2.96 (3.05 ± 0.09)</td>
</tr>
<tr>
<td>50%</td>
<td>0.623 (0.621 ± 0.002)</td>
<td>33.8 (33.6 ± 0.2)</td>
<td>73.9 (73.7 ± 0.2)</td>
<td>15.5 (15.3 ± 0.15)</td>
<td>3.00 (3.1 ± 0.1)</td>
</tr>
<tr>
<td>25%</td>
<td>0.618 (0.617 ± 0.001)</td>
<td>33.5 (33.4 ± 0.1)</td>
<td>72.4 (72.0 ± 0.4)</td>
<td>15.0 (14.85 ± 0.15)</td>
<td>3.26 (3.4 ± 0.14)</td>
</tr>
<tr>
<td>0%</td>
<td>0.612 (0.610 ± 0.002)</td>
<td>8.9 (8.6 ± 0.3)</td>
<td>29.3 (29.0 ± 0.3)</td>
<td>1.6 (1.5 ± 0.1)</td>
<td>15.2 (17 ± 1.8)</td>
</tr>
</tbody>
</table>

* Data and statistics based on five cells of each condition.

** Numbers in bold are the champion values of each condition.

Fig. 4. a) The XPS spectra for the MgOx samples post-annealed at different temperatures. b) Compound depth profiles measured with SIMS for as-deposited and annealed 10 nm MgOx on Si. c) The FTIR spectra for the MgOx samples post-annealed at different temperatures.
as shown in Fig. S5, the bulk film structure and the work function didn't change significantly. Combining with those above results, we conclude that precondition of the low work function MgO materials (2.8 eV) is sensitive to the Si–O–Mg bond.

The influence of hydrogen at the interface on the passivation quality of silicon surfaces has been studied extensively since the 1980s, and hydrogen is mainly introduced by annealing the silicon samples with a H source layer [45,46]. Hydrogen release at metal-oxide interfaces has also been studied, for examples, Al/SiO2, Pd/MgOH, Cu/MgOH interfaces [47]. Lin et al. speculated that the aluminum gate-anode might release positive hydrogen ions [48]. Huang et al. calculated that hydrogen interstitials are more likely to form at the Si–H site because of the lower formation energy, it is linked to the passivation of the non-bonding silicon sp3 orbital [48]. Rh, Co, and Cu have been reported to react with hydroxyls on alumina at room temperature [49]. The interaction between Pd and MgOH at slightly elevated temperature (390 K) due to the bad oxygen affinity of Pd has been reported [47]. Yang et al. deposited a thin Al layer on top of the TiO2 and annealed them in a forming gas ambient to improve the passivation quality of TiO2/n-Si interfaces [50]. In this work, thermally evaporated Al thin layer has been found to be effective in improving the passivation quality of the MgOx/n-Si interface, as shown in Fig. 1d. In order to understand this phenomenon, the variation of compositions and distribution at the interface were investigated using secondary ion mass spectrometry (SIMS). As shown in Fig. 5a, to distinguish the changes in the hydrogen distribution and the contribution of background hydrogen from surface contaminants, residual gas, MgOx layer and Al thin layer, annealed MgOx (200 °C)/n-Si, Al/n-Si structures were also tested as background samples. The SIMS profiles indicate that the H levels decreased towards the silicon substrate for post-annealed MgOx/Si interface. On the other hand, with a 5 nm Al film the intensity of H signal in the MgOx layer decreased with a higher H concentration at the MgOx/Si interface, which indicates that the H atoms penetrate through the film and accumulate at the MgOx/Si interface to passivate the silicon surface. According to the MgO, MgOH− and Si− depth profiles shown in Fig. 5b, it is obvious that at outer region MgO− intensity in Al/MgOx/n-Si sample decreased significantly compare with the MgOx/n-Si sample. The changes of MgOH− and H− in the MgOx/Si interface might be attributed to the reaction between the aluminum and hydroxyl ions presented in the MgOx layer. This reaction has been reported due to the release of atomic hydrogens, which then diffused across the oxide to satisfy dangling bonds at the oxide-silicon interface [50].

$$\text{Al} + \text{OH}^- \rightarrow \text{AlO}^- + \text{H}$$

All these SIMS results clearly demonstrate that the release and subsequent diffusion of atomic hydrogens from the MgOx layer toward the interface region after metalization lead to a concurrent improvement in the passivation at the MgOx/n-Si interface.

In conclusion, a simple low-temperature post-annealing and a metalization process are found to be effective in activating and optimizing the passivation effect of evaporated MgOx layers over n-Si substrates. Symmetrical sample of Al/MgOx/n-Si/MgOx/Al gave a surface recombination velocity with a low value of 14.9 cm/s which is comparable to the state-of-the-art atomic layer deposited TiOx. Dual functions of constructing Ohmic contact and passivating contact for the MgOx films have been verified. The passivation mechanism was attributed to the interfacial bond formation and hydrogen passivation. N-PERC dopant-free heterojunction solar cells were then fabricated via simple hard-masker patterning, with evaporated MgOx as both electron transporting layer as well as passivation layer. In comparison with the cells with n-Si/Al rear contacts, the PERC cells obtained great increase of Si mV, 3.6 mA/cm² and 2.9% for the Voc, Jsc and FF, respectively. The easy activating method of MgOx demonstrates the industrial feasibility of the rich reserve, low cost, non-toxic process of MgOx within the c-Si photovoltaic field. Our solutions of boosting the passivation property of MgOx as well as the novel design of contact structure obviously open up the possibility of using evaporation-processed metal oxides as effective and low-cost passivating contact choices for c-Si photovoltaic devices.

3. Experimental section

Solar Cells Fabrication: One-side polished, Czochralski, n-type (1–3 Ω cm) wafers with a thickness of 270 μm were used to fabricate PERC type dopant-free heterojunction solar cells. Randomly pyramidal structures were textured through immersing the polished side of Si wafer into mixed solutions with 2.5% KOH and 1.25% isopropanol at a temperature of 80 °C for 15 min while protecting the other side by a homemade tool. The rear side of n-Si was polished in a TMAH solution at a temperature of 80 °C for 15 min while protecting the textured side. Following the standard RCA cleaning process and short-time HF dipping to remove the oxide layer, PEDOT:PSS (PH1000 from Clevios) solution mixed with dimethylsulfoxide (DMSO, 5 wt %) and Triton-100 (0.1 wt %) was spin coated on the random pyramid surface at a thickness of approximately 80 nm and then annealed at 130 °C for 10 min.

For the rear interface, 10 nm MgOx layer was deposited on the rear side of the Si wafer from a MgO source crucible with a fixed growth rate of 0.2 Å/s at ambient temperature by electron-beam evaporation via a hard grid mask. After that, full-area 1 nm MgOx was deposited onto the rear side with the same process, followed by post-annealing at 250 °C for 10 min in air. Afterward, Al back electrode with a thickness of 300 nm and Ag front electrode (7% coverage) with a thickness of 300 nm were deposited by thermal evaporation in sequence. After cell fabrication, water-insoluble DEP [51], dissolved in acetone solution with a mass fraction of 50% was spin coated upon the cells to enable the fully conformal contact in heterojunction portions. The thickness of the DEP layer is about 1 μm.

![Fig. 5. a) Total amount of hydrogen depth profiles measured with SIMS for post annealed 10 nm MgOx at 200 °C (10 min) on Si, 5 nm Al/post annealed 10 nm MgOx at 200 °C (10 min) on Si and 5 nm Al on Si. b) Compound depth profiles measured with SIMS for post annealed 10 nm MgOx on Si and 5 nm Al/post annealed 10 nm MgOx on Si and the intensity ratio before and after Al deposition.](image-url)
Characterization: The PV performance was measured using a Class AAA solar simulator (Oriel, Sol3A) with a Xe-arc lamp under Air-mass 1.5 illumination (1000 W m⁻²) in the standard testing condition. The illumination intensity was calibrated using an encapsulated Si cell from Newport Corporation. The cells were shielded by an opaque mask with a designated aperture area of 0.7 cm². The external quantum efficiency curves were measured by a quantum efficiency measurement system (Newport Oriel, IQE-200) and Sinton WCT-120 lifetime tester using transient (PCD) or quasi-steady-state photocurrent density methods. Transmittance was performed with a 150-mm-diameter integrating sphere by excluding those of the substrate (PerkinElmer Lambda, 950 UV/Vis/NIR). Time-of-flight secondary ion mass spectroscopy (ToFSIMS) depth profiling (ION-TOF Model IV, Ion-Tof GmbH, Münster, Germany) was performed by sputtering samples with AuGa⁺ ions (1 keV) under high vacuum (3 × 10⁻⁸ mbar). XPS was performed.

References


Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2019.05.015.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (61874177, 61674154, 61474144, 61574145), Major State Basic Research Development Program of China (No. 2016YFB0700700), Zhejiang Provincial Natural Science Foundation (LR16F040002, LR15F040003), Major Project and Key S&T Program of Ningbo (2016B10004), Natural Science Foundation of Zhejiang (LR16F040002, LR19E020001, LY15F040003), Major State Basic Research Development Program of China (No. 2015CB932000), Zhejiang Provincial Natural Science Foundation (LR16F040002, LR15F040003), Ningbo (2015A610040, 2017A610020, 2017A610103).

Jing Yu received her B.S. degree in Material Forming and controlling Engineering from Shandong University, Shandong, China, in 2014. She is currently working toward the Ph.D. degree with the Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Science, Ningbo, China. Since 2018 she studied at the Australian National University as a visiting student. Her research interests focus on high efficiency heterojunction solar cells with metal oxides as carrier-selective contacts.
Mingdun Liao received the B.S. degree in microelectronics and the master's degree in condensed matter physics from Shandong University, Shandong, China, in 2006 and 2009, respectively. He is currently an engineer with the Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo, China. His current research interests include the novel crystalline silicon solar cell process towards industrial application.

Di Yan received his PhD degree from the Australian National University in 2016. Since then, he has been working at the ANU as a research fellow. His research interests include development of advanced passivating contact technologies and fabrication of high efficiency silicon solar cells. He has published over 50 journal papers.

Yimao Wan received his B.E. degree from the Nanyang Technological University, Singapore in 2004, and PhD degree from the Australian National University in 2014. Since then, he has been working at the ANU as a research fellow, coordinating a large ARENA-Trina project (~$2 million) from grant application to daily activity management. He has a proven track-record of 60 scientific publications in international conferences and peer-reviewed journals. His research interests include surface passivation, carrier selective contacts, silicon solar cells, perovskite/Si tandem cells and photovoltaic based photoelectrochemical water splitting.

Hao Lin received his B.S. and M.S. degree in faculty of Science from Ningbo University, China, in 2010 and 2013, respectively. From 2012 to 2015, he worked in department of Physics and Materials Science, City University of Hong Kong. Currently, he is a Ph.D. candidate at School of Physics and Astronomy, Shanghai Jiao Tong University. His research interests include the solar energy materials, anti-reflection structure and dopant-free all-back-contact solar cells.

Zilei Wang received his B.S. degree in College of Physics and Information Engineering at Fuzhou University, China, in 2015. He is involved in a joint program between University of Science and Technology of China and Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences (CAS) in Ningbo, China. His research interests focus on organic-inorganic hybrid solar cells.

Pingqi Gao received Ph.D. degrees in Department of Physics from Lanzhou University in 2010. From 2007 to 2011, he worked in Nanyang Technological University as a visiting researcher and a research staff. In 2013, he worked at Ningbo Institute of Materials Technology and Engineering, CAS, as an associate professor and then a professor (2015). He joined Sun Yat-sen University in 2018. His research focus on high efficiency solar cell technology, especially on developing new materials and processes for solar energy conversion. He has published over 70 journal papers and serves as an active referee for 20 journals.

Yuheng Zeng received Ph.D. degrees in State Key Laboratory of Silicon Materials from Zhejiang University in 2010. Since graduation, he joined Ningbo Institute of Materials Technology and Engineering, CAS, as a postdoc research fellow and then an associate professor (2013). In 2015, he worked at the Australian National University as a visiting scholar. His research focus on high-efficiency solar cells with passivated tunneling contacts and industrial technologies and high efficiency tandem solar cells. He has published over 40 journal papers and applied more than 20 patents.

Baojie Yan earned his Ph.D. from Nankai University, China, in 1989, during which he did a part of his PhD thesis in Tokyo Institute of Technology, Japan. After graduation he worked in Erlangen University, Germany, Catholic University of Leuven, Belgium, the University of Utah, USA. He started his industrial career in 1998 in photovoltaic solar energy, thin film transistors for display, and other optoelectronics. He joined Ningbo Institute of Materials Technology and Engineering, CAS in 2017. Dr. Yan has authored over 200 publications. His research interests include HIT and TOPCon solar cells with the emphasis of transferring the lab learnt technology to industrial applications.

Jichuan Ye received the B. S. degree in Materials Science and Engineering from University of Science and Technology of China in 2001 and the Ph.D degree in Materials Science from University of California, Davis, USA in 2005. He joined Ningbo Institute of Material Technology and Engineering, CAS, as a professor and Ph.D. advisor since August of 2012. He was awarded for "Thousand Young Talents Program of China" in 2012. He has published more than 60 publications with nearly 500 times citations, applied more than 40 patents (including 10 awarded patents).