Molybdenum oxide MoO$_x$: A versatile hole contact for silicon solar cells

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This letter examines the application of transparent MoO$_x$ (x < 3) films deposited by thermal evaporation directly onto crystalline silicon (c-Si) to create hole-conducting contacts for silicon solar cells. The carrier-selectivity of MoO$_x$ based contacts on both n- and p-type surfaces is evaluated via simultaneous consideration of the contact recombination parameter $J_{0c}$ and the contact resistivity $\rho_c$. Contacts made to p-type wafers and p$^+$ diffused regions achieve optimum $\rho_c$ values of 1 and 0.2 m$\Omega$·cm$^2$, respectively, and both result in a $J_{0c}$ of $\sim$200 fA/cm$^2$. These values suggest that significant gains can be made over conventional hole contacts to p-type material. Similar MoO$_x$ contacts made to n-type silicon result in higher $J_{0c}$ and $\rho_c$ with optimum values of $\sim$300 fA/cm$^2$ and 30 m$\Omega$·cm$^2$ but still offer significant advantages over conventional approaches in terms of contact passivation, optical properties, and device fabrication. © 2014 AIP Publishing LLC.

The spatial separation of light-generated electron-hole pairs is critical to the functionality of all photovoltaic devices. The segregation of electrons and holes towards their respective contact regions requires the formation of pathways of asymmetric electron and hole conductivity. The majority of crystalline silicon (c-Si) solar cells achieve this by introducing a high concentration of dopants (usually phosphorus, aluminium, or boron) in the near-surface regions of the c-Si wafer. The dopant species increase the concentration of (and hence, conductivity for) one charge carrier, whilst having the opposite effect for the other. This approach is particularly advantageous for directly metalized silicon contacts as the metal-silicon interface suffers from both large majority carrier resistance and high minority carrier recombination, both of which can be reduced by heavy surface doping. However, the high majority carrier concentration within the doped regions also causes significant Auger recombination, introducing a fundamental limit on the possible reduction of recombination. The lowest recombination parameters for heavily doped, metal-contacted regions have experimentally been found to be $\sim$300 fA/cm$^2$ for phosphorus, $\sim$400 fA/cm$^2$ for boron, and higher still for aluminium alloyed regions ($J_0$ values have been adjusted in accordance with the intrinsic carrier concentration used in this letter $n_i = 8.6 \times 10^{17}$cm$^{-3}$). This limitation has prompted the development of device designs with small contact fractions where the total minority carrier recombination can be reduced at the expense of increased majority carrier resistance—a trade-off which is usually permissible given their relative impact on solar cell performance. However, difficulties associated with the transfer of small contact fractions to industrial pilot lines have led to research into alternative means of separating carriers and contacting solar cells.

An alternative strategy to achieve carrier-selectivity is via the application of thin layers of materials on the c-Si absorber that provide an asymmetry in carrier conductivity. Cell architectures utilising such materials have recently demonstrated world record efficiencies on c-Si, outperforming their dopant diffused counterparts. Not surprisingly, research into suitable electron and hole collecting layers on c-Si is currently a popular topic, with some groups transferring layers commonly used for the same purpose from non-c-Si based solar cells. For example, organic polymer, transition metal oxide, and transparent conductive oxide based contacts, which are standard in other photovoltaic technologies, have recently been demonstrated on c-Si. Among these contacting schemes, the use of sub-stoichiometric molybdenum oxide MoO$_x$ (x < 3) stands out as particularly attractive given its ease of deposition and already demonstrated performance on c-Si. This letter examines the application of MoO$_x$ directly to c-Si to create a hole-transporting contact for c-Si solar cells.

Molybdenum trioxide MoO$_3$ is a wide band-gap material ($\sim$3 eV) with an exceptionally large electron affinity ($\sim$6.7 eV) and ionisation energy ($\sim$9.7 eV). When deposited by vacuum evaporation from a solid MoO$_3$ source, as is the case in this letter, a slightly sub-stoichiometric (MoO$_x$, x<3) amorphous film results. The reduced Mo oxidation state results in the formation of a defect band below the conduction band and provides the film with a semi-metallic, n-type character. The conductivity of MoO$_x$ films has been shown to vary by more than ten orders of magnitude in transitioning from the insulating MoO$_3$, with reported conductivities as low as $10^{-7}$ S/cm, to the semi-metallic MoO$_2$ which exhibits conductivities in the range of $10^3$ S/cm. Gains in conductivity are typically weighed against transparency and work function—both of which are found to decrease with a decreasing oxidation state.

The most significant characteristic of thermally evaporated MoO$_x$ films is their large chemical potential of up to $\sim$6.9 eV—much higher than that of the elemental metals, a characteristic that they share with two other sub-stoichiometric transition metal oxides: VO$_x$ and WO$_x$. Amongst these three oxides, MoO$_x$ has the additional advantage of a low melting point, which assists in maintaining a high oxidation state and a low thermal budget when evaporating.

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When MoO$_x$ is applied to c-Si, the large chemical potential difference between the two materials induces a balancing electrostatic potential which falls partially across both materials and, if Fermi-level pinning is present, across the interface. Whilst Fermi-level pinning is pervasive at elemental metal/c-Si interfaces, it is still unknown to what extent it affects the MoO$_x$/c-Si interface, and it has recently been suggested that MoO$_x$ can partially alleviate this effect for transition-metal dichalcogenides.\textsuperscript{17} In the event of weak or no Fermi-level pinning at the MoO$_x$/c-Si interface, a hole accumulation layer on p-type c-Si and a hole inversion layer on n-type c-Si would be expected—facilitating low resistance hole transport out of the c-Si absorber.

In this letter, the application of MoO$_x$ to c-Si is investigated to form simple hole contacts in three different configurations. These are categorised as “accumulation” type contacts to (i) lightly doped p-type silicon (referred to hereafter as $p$Si/MoO$_x$ contact), (ii) heavily boron doped silicon (referred to hereafter as $p^+$Si/MoO$_x$ contact), and (iii) an “inversion” type contact to low resistivity n-type silicon (referred to hereafter as $n$Si/MoO$_x$ contact).

The efficacy of the $p$Si/MoO$_x$, $p^+$Si/MoO$_x$, and $n$Si/MoO$_x$ hole contacts, that is, their selectivity towards holes, is assessed via their recombination and resistive properties. The contact recombination parameter $j_{dc}$ (as determined from carrier lifetime test structures) provides information on the undesired “conductivity” presented to electrons towards the c-Si/MoO$_x$ interface, whilst the contact resistivity $\rho_c$ (as determined from contact resistance test structures) indicates the detrimental resistance to holes. Improved hole-selectivity is achieved via simultaneous minimisation of $j_{dc}$ and $\rho_c$.

All test structures were fabricated on (100) oriented, float-zone, c-Si substrates. The wafer resistivities of the $p$Si/MoO$_x$ and $n$Si/MoO$_x$ structures were $\sim$2.1 $\Omega$·cm and $\sim$4.2 $\Omega$·cm, respectively, whilst the $p^+$Si/MoO$_x$ contact structures were fabricated on 100 $\Omega$·cm n-type wafers with front and rear surface boron diffusions (surface concentration $N_{surf} \sim 1 \times 10^{19}$ cm$^{-3}$ and sheet resistance $R_{sh} \sim 110 \Omega/\square$). Test structures were RCA cleaned and immersed in a 1% HF solution immediately prior to MoO$_x$ deposition. MoO$_x$ films of 3–80 nm thickness were thermally evaporated at a rate of 1Å/s from a MoO$_3$ powder source (99.95% purity) with a base pressure of $<10^{-7}$ Torr.

Lifetime test structures were prepared by depositing MoO$_x$ on both wafer surfaces. A thin palladium (Pd) ($<10$ nm) over-layer was evaporated onto the MoO$_x$ to mimic a device contact, whilst still allowing sufficient light transmission for the injection dependent carrier lifetime to be measured by the photoconductance decay technique. The $j_{dc}$ values were extracted from the measured effective carrier lifetimes using the Kane and Swanson technique\textsuperscript{19} with an $n_c$ value of $8.6 \times 10^{-19}$ cm$^{-3}$ (at 25 $^\circ$C). This technique, originally applied to characterise dopant diffusion wafer surfaces (like the $p^+$Si/MoO$_x$ contact), has been shown to also be valid for undiffused wafers with strongly inverted or accumulated surfaces,\textsuperscript{20} as is expected for the $p$Si/MoO$_x$, $n$Si/MoO$_x$, and $p^+$Si/MoO$_x$ contacts.

Contact resistance test structures were made by depositing MoO$_x$ on one side of a c-Si sample, following which a Pd (40 nm)/Al (1 $\mu$m) metal stack was evaporated on top through a shadow mask to create the desired contact structure pattern. For the $n$Si/MoO$_x$, $p^+$Si/MoO$_x$, contact structures, a transfer-length-method (TLM) contact pad array was used to measure $\rho_c$. Whilst the use of the TLM procedure on heavily diffused surfaces is well accepted,\textsuperscript{21} its application to low resistivity wafers with a surface inversion layer has only been explored briefly.\textsuperscript{22,23} In this approach, we have assumed that current flows are confined to the inversion layer. The sheet resistance of this inversion layer is also measurable by the TLM.

For the $p$Si/MoO$_x$ contacts, $\rho_c$ was measured using the method devised by Cox and Strack.\textsuperscript{24} For this measurement, an Ohmic rear contact, formed by evaporated aluminium, was assumed to contribute negligibly to the total measured resistance, rendering the extracted $\rho_c$ an upper limit for the $p$Si/MoO$_x$ $\rho_c$. All current voltage (I-V) measurements were taken in the dark using a Keithley 2425 source-meter at $\sim$23 $^\circ$C. The $\rho_c$ values presented here are without a sintering step. It should be noted that in all contact structures used in this study, the extracted $\rho_c$ comprises the resistance of the MoO$_x$/c-Si and MoO$_x$/Pd interfaces as well as the MoO$_x$ bulk resistivity. In addition, whilst Pd was used in this instance, less extensive tests revealed similar results using evaporated Ni and sputtered indium-tin-oxide (ITO) layers.

Representative I-V measurements and $\rho_c$ extractions for the three contact structures are provided in Figure 1. It can be seen that all contacts exhibit Ohmic I-V behaviour.

![FIG. 1. Current-voltage measurements and $\rho_c$ extractions for (a) $p$Si/MoO$_x$, (b) $p^+$Si/MoO$_x$, and (c) $n$Si/MoO$_x$, contact structures with a fixed MoO$_x$ interlayer thickness of $\sim$10 nm.](image-url)
allowing accurate extractions of \( \rho_c \). The correlation of the linear fits to data used in the TLM extraction of \( \rho_c \) was high, with \( R^2 \) values typically greater than 0.99.

Figure 2(a) presents the measured dependence of \( \rho_c \) on MoO\(_x\) thickness for the “accumulation” type contacts—\( pSi/\)MoO\(_x\) and \( p^+Si/\)MoO\(_x\). The \( \rho_c \) values corresponding to unannealed, directly metalized \( pSi/Pd \) and \( p^+Si/Pd \) contacts are \( \rho_c = 10 \, \text{m\( \Omega \)}\text{cm}^2 \) and \( \rho_c = 1 \, \text{m\( \Omega \)}\text{cm}^2 \), respectively. Both the \( p^+Si/\)MoO\(_x\) and \( pSi/\)MoO\(_x\) contacts show similar \( \rho_c \) trends with MoO\(_x\) thickness—an initial decrease in \( \rho_c \) relative to the directly metalized surface followed by a gradual increase for thicker MoO\(_x\) films—with a local minimum \( \rho_c \) of 1 and 0.2 m\( \Omega \)cm\(^2\) for \( pSi/\)MoO\(_x\) and \( p^+Si/\)MoO\(_x\) structures with \( \sim 10 \) and 5 nm of MoO\(_x\), respectively. The similarity between the two \( \rho_c \) numerical values and trends, despite the use of different contact test structures, support the accuracy of both measurement methods. The minimum \( \rho_c \) value for the \( pSi/MoO_x \) contact is at the resolution of the measurement technique, shown in Figure 2(a) as a horizontal green line. Therefore, we cannot, with certainty, conclude that \( \rho_c \) is lower for the \( p^+Si/MoO_x \) than for the \( pSi/MoO_x \).

A comparison between the \( \rho_c \) values measured here and the MoO\(_x/Pd\) interface resistivity (measured to be \( \sim 0.2 \, \text{m\( \Omega \)}\text{cm}^2 \) in other studies\(^{17}\)) suggests that, particularly in the case of the \( p^+Si/MoO_x \), the total resistivity may be dominated by the MoO\(_x/Pd\) interface.

The initially decreasing \( \rho_c \) seen for both “accumulation” contacts could potentially be a result of partial MoO\(_x\) surface coverage for the thinner films, as island growth (Volmer-Weber nucleation) is common for thermal evaporation. The increase in \( \rho_c \) for MoO\(_x\) thickness above 20 nm is likely a consequence of the MoO\(_x\) bulk resistivity dominating the total \( \rho_c \). From the measured \( \rho_c \) of the thicker structures (30–80 nm of MoO\(_x\)), we extract an average dark conductivity \( \sigma_d \) for the MoO\(_x\) film of \( \sim 2 \times 10^{-3} \, \text{S/cm} \), which falls towards the lower end of the range reported in the literature, indicating that the film is only slightly substoichiometric. This value is comparable to that of phosphorus or boron doped \( a-Si:H \) films implemented in silicon heterojunction (SHJ) solar cells.\(^{25}\)

An analogously plotted of the measured \( J_{oc} \) dependence on MoO\(_x\) thickness for the “accumulation” type contacts is shown in Figure 2(b). It can be seen that both MoO\(_x\) coated \( p^\text{-} \)type surfaces produce a \( J_{oc} \) of \( \sim 200 \, \text{fA/cm}^2 \) irrespective of (i) the MoO\(_x\) thickness; (ii) the surface dopant concentration (\( pSi/\)MoO\(_x\) \( \sim 6.8 \times 10^{15} \, \text{cm}^{-3} \) and \( p^+Si/\)MoO\(_x\) \( \sim 1 \times 10^{19} \, \text{cm}^{-3} \)); and (iii) the application of an overlying Pd layer. The similar \( J_{oc} \) values obtained for the two \( p^\text{-} \)type surfaces, despite their vastly different surface dopant concentrations, are consistent with the presence of a strong surface accumulation layer. This point is also supported by the similarities in \( \rho_c \) dependence on MoO\(_x\) thickness seen for the \( pSi/\)MoO\(_x\) and \( p^+Si/\)MoO\(_x\) contacts in Figure 2(a). Regardless of the underlying mechanisms, the almost identical \( J_{oc} \) and \( \rho_c \) behaviour presented above for the \( pSi/MoO_x \) and \( p^+Si/MoO_x \) contacts demonstrates that the MoO\(_x\) layer removes the necessity of the boron diffusion.

Figures 3(a) and 3(b) show the measured dependence of \( \rho_c \) and the (dark) inversion layer sheet resistance \( R_{IL} \) on...
MoO\textsubscript{x} thickness for the \textit{n}Si/MoO\textsubscript{x} “inversion” type contact. A \(\rho_c\) value for the directly metalized surface could not be measured by the TLM technique due to the absence of a surface inversion layer; however, it is known that making direct metal contact to n-type c-Si of moderate resistivity is technologically challenging. Similar to the \(\rho_c\) trend in Figure 2(a), an initial decrease in \(\rho_c\) with MoO\textsubscript{x} thickness is observed, again potentially associated with Volmer-Weber nucleation. After this strong initial reduction, \(\rho_c\) decreases slowly from \(\sim 150\ \text{m}\Omega\cdot\text{cm}^2\) to \(30\ \text{m}\Omega\cdot\text{cm}^2\) before increasing in the thickness range of 40–80 nm to a similar \(\rho_c\) to that seen for the \textit{p}Si/MoO\textsubscript{x} and \textit{p}++Si/MoO\textsubscript{x} contacts.

As shown in Figure 3(b), the magnitude of \(R_{\text{IL}}\) initially decreases with MoO\textsubscript{x} thickness, consistent with partial surface coverage, before saturating at \(\sim 12\ \text{k}\Omega\Box\). This sheet resistance is approximately two orders of magnitude higher than the sheet resistance of the n-type Si wafer (\(\sim 150\ \Omega\Box\)), which confirms that the current flow is confined to the inversion layer by the carrier depletion region formed between it and the n-type substrate, hence supporting the applicability of using the TLM to measure this contact. The \(R_{\text{IL}}\) \(\sim 12\ \text{k}\Omega\Box\) measured here is lower than the values reported for inversion layer solar cells, suggesting a higher concentration of holes near the surface.\(^{22,23}\)

An equivalent inversion layer charge can be calculated from \(R_{\text{IL}}\) using an average surface hole mobility of 80 cm\textsuperscript{2}/V s, taken from the previous studies on MOSFET devices.\(^{26}\) From this charge, a corresponding potential at the c-Si surface \(\psi_s\) can be calculated by assuming Fermi-Dirac statistics. Under these assumptions, \(\psi_s\) is calculated to be \(-0.92\ \text{V}\), with a corresponding hole surface concentration of \(\sim 8.6 \times 10^{19}\ \text{cm}^{-3}\).

The \(J_{\text{oc}}\) measurements for the \textit{n}Si/MoO\textsubscript{x} contact as a function of the MoO\textsubscript{x} thickness shown in Figure 3(c) follow a similar trend to those in Figure 2(b): \(J_{\text{oc}}\) is approximately independent of the MoO\textsubscript{x} thickness. The non-metalized \textit{n}Si/MoO\textsubscript{x} structures achieve a minimum \(J_{\text{oc}}\) of \(\sim 200\ \text{fA/cm}^2\), which increases to \(\sim 300\ \text{fA/cm}^2\) after Pd deposition.

To contextualise these results, it is illustrative to compare them with conventional aluminum and boron \textit{p}+ hole contacts. The Al alloyed \textit{p}+, formed by rapid melting and recrystallization of the c-Si/Al interface, is typically applied as a rear contact to a \textit{p}+type wafer and hence is comparable to the \textit{p}Si/MoO\textsubscript{x} contact. The relatively low Al dopant concentration (limited by a solid solubility of \(\sim 3 \times 10^{18}\ \text{cm}^{-3}\) (Ref. 27)) and the formation of recombination active point defects within the Al doped region generally limit the \(J_{\text{oc}}\) to between 600 and 900 fA/cm\textsuperscript{2}.\(^{2,4,28}\) although lower values have been reported.\(^{29}\) Corresponding \(\rho_c\) values of 1 to 50 m\Omega\cdot\text{cm}^2 have been measured for this hole contact.\(^{30,31}\) The \textit{p}Si/MoO\textsubscript{x} produces lower \(J_{\text{oc}}\) values for a wide range of MoO\textsubscript{x} thicknesses and matches the best reported Al alloyed \(\rho_c\) values. The results in this study are especially significant given the moderate doping level of the wafers used for the \textit{p}Si/MoO\textsubscript{x} contacts—suggesting that it may be possible to achieve a lower \(\rho_c\) on wafers with an even lower doping level, thus mitigating issues such as light-induced bulk lifetime degradation.\(^{32}\) Improved optical performance, reduced process thermal budget, and the ease by which partial contacts can be applied are all further possible advantages of the \textit{p}Si/MoO\textsubscript{x} contact structure.

The boron \textit{p}+ contact, typically formed by high temperature (>900 °C) thermal diffusion and subsequent metallization, is the standard hole contact for \textit{n}+type c-Si solar cells and hence can be compared to the \textit{n}Si/MoO\textsubscript{x} contacts presented in this study. Optimised \(J_{\text{oc}}\) - \(\rho_c\) combinations of 400 fA/cm\textsuperscript{2} and \(\sim 0.1\ \text{m}\Omega\cdot\text{cm}^2\) can be achieved for metal-contacted heavily doped boron diffused \textit{p}++ contacts.\(^{3,33}\) In comparison, the optimal \(J_{\text{oc}}\) obtained for the \textit{n}Si/MoO\textsubscript{x} contact is lower, \(J_{\text{oc}}\) \(\sim 300\ \text{fA/cm}^2\), but the \(\rho_c\) value of \(\sim 30\ \text{m}\Omega\cdot\text{cm}^2\) is considerably higher. Despite that the \textit{n}Si/MoO\textsubscript{x} contact is still adequate for large-area contacts. We have tested such \textit{n}Si/MoO\textsubscript{x} contact via a rudimentary ITO/MoO\textsubscript{x}/c-Si (n/poly-Si(n+)) device with a planar front surface and coarse front contact grid—achieving an open-circuit voltage of \(\sim 640\ \text{mV}\) measured by the Suns-V\textsubscript{oc} technique,\(^{34}\) which is consistent with the \(J_{\text{oc}}\) value given above. The obtained results for the \textit{p}++Si/MoO\textsubscript{x} also suggest that a partial MoO\textsubscript{x} contact could be applied on a light boron diffusion to supersede the selective \textit{p}++ contact approach with improved recombination characteristics and simplified processing.

A remaining challenge is the temperature stability of \(J_{\text{oc}}\), which degrades at low temperatures, similar to that found for silicon heterojunction cells. This stability can be improved by the addition of an interlayer, which has also been shown to further improve surface passivation.\(^{10}\)

In conclusion, thin films of MoO\textsubscript{x} deposited by thermal evaporation form excellent hole-selective contacts on both \textit{p}+type and \textit{n}+type c-Si. The passivation quality of the contacts is independent of the MoO\textsubscript{x} thickness, with \(J_{\text{oc}}\) values of \(\sim 200\) and \(\sim 300\ \text{fA/cm}^2\) for \textit{p}- and \textit{n}-type surfaces, respectively. Conversely, \(\rho_c\) is found to be strongly dependent on MoO\textsubscript{x} thickness. Upper-limit \(\rho_c\) values of 1 and 0.2 m\Omega\cdot\text{cm}^2 have been demonstrated on \textit{p} and \textit{p}+ surfaces, respectively. The \(\rho_c\) on \textit{n}-type surfaces is higher, with an optimum value of \(\sim 30\ \text{m}\Omega\cdot\text{cm}^2\), though still applicable to c-Si solar cell designs. It is clear that MoO\textsubscript{x} films can play a significant role in the development of selective-contacts both in terms of versatility and performance.

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