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Atomic-layer deposited Nb$_2$O$_5$ as transparent passivating electron contact for c-Si solar cells

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**A B S T R A C T**

Passivating contacts based on metal oxides have proven to enable high energy conversion efficiencies for crystalline silicon (c-Si) solar cells at low processing complexity. In this work, the potential of atomic-layer deposited (ALD) Nb$_2$O$_5$ as novel electron-selective passivating contact is explored in terms of recombination parameter $J_0$ and contact resistivity $\rho_c$. It is shown that after forming gas annealing, ALD Nb$_2$O$_5$ can provide adequate surface passivation with $J_0$ values down to 25–30 fA/cm$^2$. On HF-treated c-Si surfaces a minimum film thickness of ~ 3 nm is required to achieve this high level of passivation, whereas on surfaces with a wet-chemical SiO$_2$ interlayer the high passivation level is persistent down to film thicknesses of only 1 nm. Ohmic n-type contacts have been achieved using Al as contacting metal, where annealing the samples after Al contacting proved crucial for obtaining good contact properties. Low contact resistivity values of 70 and 124 m$\Omega$cm$^2$ for 1 and 2 nm Nb$_2$O$_5$ films, respectively, have been achieved on c-Si substrates that received an HF treatment prior to Nb$_2$O$_5$ deposition. Transmission electron microscopy imaging shows that on such surfaces the annealing treatment leads to the formation of a (1.7 ± 0.2) nm interfacial oxide in between the c-Si substrate and the Nb$_2$O$_5$ film. The presented results demonstrate the potential of ALD Nb$_2$O$_5$ as electron-selective passivating contact and directions for future research are outlined.

1. Introduction

Passivating contacts have in recent years proven to be vital building blocks for high-efficiency crystalline silicon (c-Si) solar cells [1,2]. Passivating contacts, which typically consist of a stack of nanolayers, form the electron- and hole-selective contacts to silicon by (i) effectively passivating the c-Si surface, and by (ii) exhibiting a strong asymmetry in the conduction for electrons and holes, with the conductivitity for the majority carrier (i.e., the carrier to be extracted) being sufficiently high [3]. These two requirements are met if [1,4]:

- A low surface recombination parameter $J_0$ is measured, since this implies a well-passivated surface. If the $J_0$ remains low after metallization, it means that at least one carrier type is shielded from the metal contact, since otherwise strong recombination would occur at the metal contact.
- A low contact resistivity $\rho_c$ is measured, which implies that at least one carrier type can reach the metal contact without excessive Ohmic losses.

Although there are some caveats to using solely $J_0$ and $\rho_c$ to assess the electrical performance of a passivating contact (see e.g. Ref. [5]), it is a useful and facile way of assessing the efficiency potential. The influence of $J_0$ and $\rho_c$ on the simulated efficiency potential of an otherwise ideal c-Si solar cell is shown in the contour plot of Fig. 1, adapted from reference [1]. As can be seen, a lower $J_0$ contributes strongly to a higher efficiency, mainly by an increase in open-circuit voltage $V_{oc}$, whereas a $\rho_c$ below ~ 0.3 $\Omega$cm$^2$ is required to prevent Ohmic losses from adversely affecting the fill factor.

As can also be seen in Fig. 1, passivating contacts based on stacks of intrinsic and doped amorphous silicon (i.e. classical silicon heterojunction (SHJ)) [6], as well as contacts based on ultrathin SiO$_x$/doped poly-Si (often coined TOPCon [7] or POLO [8]), have been the most successful both in terms of $J_0$ and $\rho_c$ as well as efficiency. Although the success of these two approaches is hard to dispute, these doped Si materials do suffer from a relatively low optical transparency [9-11]. As such, the highest cell efficiencies of over 26% for these types of contacts have been reached using the more complex interdigitated back contact (IBC) structures [6,12]. In addition, the limited thermal...
stability of a-Si:H, and especially p-type a-Si:H, render SHJ cells incompatible with fire-through metallization schemes and conventional pastes [13,14].

These considerations have warranted the search for alternative carrier-selective materials, with the goal of finding materials that exhibit e.g. higher transparency or higher stability [15]. Many of the recently-explored materials are either metal oxide- or metal fluoride-based passivating contacts, with notable examples being TiOx [16–18], MgOx [19], MoOx [20–22], WOx [23–25], V2O5 [23,26], LiF [27,28], and MgF2 [29]. Rather than relying on heavy doping, these more novel materials mostly achieve asymmetric carrier conductivity through other physical principles such as induced band bending arising from work function differences or suitable band offsets to c-Si [1,3,5,30]. As Fig. 1 also shows, these more novel approaches typically do not yet yield as good $J_0$ and $\rho_c$ values as doped a-Si:H and poly-Si. Yet, due to their higher band gap these materials do have the advantage of enhanced transparency. This is shown in Fig. 2, where the spectral absorption coefficient of a selection of these materials, as well as those of a-$\text{Si:H}$ and poly-$\text{Si}$, are compared to MoOx, TiOx, and MgF2. ALD Nb2O5, the material of this study, has been added. The refractive index $n$ and extinction coefficient $k$ of ALD Nb2O5 can be found in Fig. S1 of the Supplementary information. As can be seen, the metal oxide- and metal fluoride-based contacts clearly provide higher transparency. This stems from their higher band gaps, which are 2.9, 3.3, 3.4 eV for ALD MoOx, TiOx and Nb2O5, respectively, and 10.8 eV for MgF2 [31,32]. Besides the benefit of enhanced transparency, some of the novel materials can potentially lead to solar cell processing simplifications, as these very thin materials can often be deposited by atmospheric pressure deposition processes such as spatial ALD, which has already found its way into high-volume solar cell manufacturing [33].

In this work, Nb2O5 prepared by ALD is explored as a novel electron-selective passivating contact material. As will become clear from this work, there are very strong similarities between ALD Nb2O5 and TiOx, both in terms of their material and contacting properties, as well as in their history in solar cells. Historically, TiOx has been a commonly-employed antirefection coating in c-Si solar cells due to its suitable refractive index and low optical absorption [38]. However, since TiOx was not known for its ability to passivate the c-Si surface (and bulk) it was replaced by SiNx in the early 1990s [39]. In addition, TiOx is a common building block in organic and perovskite-based solar cells, where it is used as electron transport layer (ETL) due to its favorable band alignment with the absorber material [40,41]. The interest from the c-Si community was regained when Avasthi et al. demonstrated that TiOx can also form an electron-selective contact to c-Si arguably due to its low conduction band (CB) and high valence band (VB) offsets [30]. However, the efficiency of 7% was not state-of-the-art, and most likely limited by a lack of surface passivation. One year later, it was demonstrated by Liao et al. that TiOx prepared by ALD can actually yield a high level of surface passivation [16]. The passivation level was shown to improve through light-soaking, which was tentatively attributed to an increased negative charge density $Q_i$ by charge injection [16]. From then on, there has been a stark and rapid increase in efficiency of these contacts up to 22.1% nowadays [17]. It was shown by TEM imaging that the Al overlayer, plays a key role in forming the contact by drawing oxygen from the TiOx layer [42]. Further improvements to the contact have been enabled by using a tunnel SiO2 layer grown by thermal oxidation (TO) for passivation [17,18], and contacting by low-work-function metals to improve the downward band bending [43]. Besides yielding a respectable efficiency at low processing complexity, these contacts have also been shown to be quite thermally stable during firing, albeit under slightly milder firing conditions [17].

Although not as common as TiO2, Nb2O5 has also been used both as ARC in c-Si solar cells [44] and as ETL in perovskite solar cells [45,46] due to its very similar optical properties and band offsets as TiOx, respectively. We have recently demonstrated that ALD Nb2O5 can also very effectively passivate c-Si [47]. Part of the effective surface passivation was attributed to a negative fixed charge density of $\sim 1 \times 10^{12}$ cm$^{-3}$. Also, as was the case for TiOx, the passivation of Nb2O5 could be further enhanced by light-soaking, and the use of a thin wet chemically-grown SiO2 layer proved beneficial for the passivation performance.

In this work, the potential of ALD Nb2O5 as passivating electron-selective contact for c-Si is explored. This is motivated by the use of Nb2O5 as ETL in perovskite cells, as well as the reported electron affinity values of Nb2O5 that lie in a typical range of 3.9–4.3 eV [48–50], which is very similar to the electron affinities of TiO2, which are reported to be $\sim 4$ eV [50]. Moreover, Hoffediz et al. have recently directly compared the conduction band position of ALD TiO2 and ALD Nb2O5 using the same ALD precursor as in this work [51]. They found a small conduction band edge difference of 150 meV in the as-deposited state, which reduced to only 40 meV after annealing at 500 °C.
Therefore, it is probable that the Nb$_2$O$_5$/c-Si interface exhibits a similarly small conduction band and large valence band offset as the TiO$_x$/c-Si interface, which would facilitate selective electron transport. Indeed, in this work it will be shown that ALD Nb$_2$O$_5$ contacted by Al can yield a sufficiently low contact resistivity to c-Si for passivating contact applications. In addition, the interfacial oxide through which this electrical transport takes place has been visualized by transmission electron microscopy. Finally, we discuss opportunities for ALD Nb$_2$O$_5$ as passivating contact material and outline directions for future improvements and further research.

2. Experimental section

Nb$_2$O$_5$ thin films were prepared by thermal atomic layer deposition (ALD) using (tert-butylimido)-tris(diethylamino)-niobium ((CH$_3$)$_3$CNNb(N(C$_2$H$_5$)$_2$)$_3$, TBTDEN) as precursor and H$_2$O as reactant in an Oxford Instruments FlexAL reactor. The deposition temperature was varied between 150 and 300 °C, over which the growth-per-cycle decreases from 0.40 to 0.25 Å. 3 Ω cm floatzone n-type silicon (100) wafers were used as substrates. Prior to deposition, the oxide grown by Radio Corporation of America (RCA) cleans 1 and 2 was either removed by dipping in 1% HF for one minute or was purposely left on the wafer [52]. Spectroscopic ellipsometry (SE) measurements revealed a thickness of ~ 1.3 nm for this wet-chemical oxide grown by the RCA cleans. Spectroscopic ellipsometry (SE) measurements revealed a thickness of ~ 1.3 nm for this wet-chemical oxide grown by the RCA cleans. Post-deposition annealing treatments were carried out in a Jipelec rapid thermal anneal at 300 °C in a forming gas (10/90H$_2$/N$_2$). A Sinton WCT-120TS QSSPC setup was used to evaluate the passivating interface of Nb$_2$O$_5$ contacted by Al can yield sufficiently low contact resistivity to c-Si for passivating contact applications. In addition, the interfacial oxide through which this electrical transport takes place has been visualized by transmission electron microscopy. Finally, we discuss opportunities for ALD Nb$_2$O$_5$ as passivating contact material and outline directions for future improvements and further research.

In order to gain further insights into the passivating interface, the interface between ALD Nb$_2$O$_5$ and c-Si has been imaged by cross-sectional TEM. The visualized Nb$_2$O$_5$ layer was prepared on HF-treated c-Si at 150 °C and subjected to a 15 min 300 °C FGA treatment. For capping purposes, an ITO layer was sputtered on top of the Nb$_2$O$_5$ layer. As can be seen in Fig. 4, a (1.7 ± 0.2) nm interfacial SiO$_x$ layer is formed. In previous work, X-ray photoelectron spectroscopy (XPS) studies showed that this SiO$_x$ layer mostly forms during post-deposition annealing of the sample at 300 °C and that this SiO$_x$ layer is strongly substoichiometric. Specifically, it is closer to SiO$_{1.5}$ than it is to stoichiometric SiO$_2$ [47].

In order to evaluate the contact resistivity $\rho_c$ of ALD Nb$_2$O$_5$, samples in the so-called Cox and Strack configuration were prepared [54]. A schematic of the employed sample structure can be found in Fig. 5(a). The rear side of the samples features an Ohmic contact consisting of n-Si (n$^-$)/Al. ALD Nb$_2$O$_5$ films with a thickness of 1–4 nm were deposited onto HF-treated surfaces. Given the fact that the best passivation on HF-treated surfaces is obtained at a deposition temperature of 150 °C, this deposition temperature was also used for the evaluation of the contact resistivity. Al dots of varying diameter were evaporated onto the Nb$_2$O$_5$ films. Fig. 5(b) shows the extracted contact resistivity $\rho_c$ values prior to annealing of the structure. Reasonably low contact resistivity $\rho_c$ values of 0.10 and 0.21 Ω cm$^2$ are obtained for 1 and 2 nm-thick films, respectively. For thicker films, the IV-characteristics were highly non-Ohmic and the contact resistivity could thus not be extracted. Also, when the Al dots were directly applied to the Si, a highly non-Ohmic contact was formed. This is often attributed to Fermi-level pinning at the interface, which leads to the formation of a Schottky barrier despite the relatively low work function of Al ~ 4 eV. The proper contacting behavior observed when using Nb$_2$O$_5$ suggests that the Nb$_2$O$_5$ film is effective at depinning the Fermi level.

In order to improve the contacts, the samples were subjected to an annealing treatment. A 15 min anneal in forming gas at 300 °C was chosen, as this previously showed to yield good passivation on HF-treated surfaces [47]. The extracted contact resistivity $\rho_c$ values after annealing of samples with varying Nb$_2$O$_5$ film thickness are also shown in Fig. 5(b). The corresponding measured resistance values for the various Nb$_2$O$_5$ thicknesses as a function of the inverse dot diameter and the accompanying fits to the data used to extract the contact resistivity $\rho_c$ can be found in Fig. S3 of the Supplementary information. As can be clearly seen, the contact resistivity $\rho_c$ values improve, and could now be determined for all the examined film thicknesses. A contact resistivity $\rho_c$ of 0.070 Ω cm$^2$ is obtained for the 1 nm Nb$_2$O$_5$ film, whereas the 2 nm Nb$_2$O$_5$ film yields a slightly higher contact resistivity $\rho_c$ of 0.124 ± 0.02 Ω cm$^2$. These values are well in the relevant range of passive contacts of $\rho_c \lesssim 0.3 \Omega \text{cm}^2$. For films thicker than 2 nm, the contact resistivity is observed to rapidly increase and reaches values exceeding those relevant for passivating contact applications. For reference,
literature values for other electron-selective contacts are shown in Fig. 5b as well. As can be seen, other non-conductive electron-selective passivating contacts such as TiO$_x$ and MgF$_2$ display a similar exponential increase in contact resistivity with film thickness, which points to a tunneling-based transport mechanism. This is in contrast to electron-selective contacts based on conductive MgO$_2$, which due to the bulk conductivity of MgO$_2$, exhibit a relatively low contact resistivity for MgO$_2$ film thicknesses up to even 60 nm [19]. As can be seen, the contact resistivity values of Nb$_2$O$_5$ are somewhat higher compared to the other selective contacts. However, as is shown in the legend, it should be noted that the contact resistivity results for Nb$_2$O$_5$ were obtained on wafers with a significantly lower base doping (3 Ω cm). Using wafers with an increased base doping level typically results in a significant decrease of the contact resistivity, as was for example observed by Bullock et al. for LiF$_x$-based electron-selective contacts [27].

The TEM image in Fig. 4 revealed that a ~ 1.7 nm interfacial SiO$_x$ layer is formed after annealing. This ~ 1.7 nm SiO$_x$ is relatively thick in comparison to other interfacial oxides in passivating contacts. A 1.2 nm SiO$_2$ layer grown by thermal oxidation was used in the 21.6% efficient TiO$_x$-based cell of Yang et al. [55] TEM imaging in that work also shows the interfacial oxide for TiO$_x$ prepared on HF-treated c-Si and subjected to a 250 °C FGA treatment. Although the thickness of the interfacial oxide is not specified in that case, it is ostensibly thinner than the 1.2 nm oxide grown by thermal oxidation. Furthermore, the typical oxide thickness in TOPCon structures based on tunnel SiO$_2$/poly-Si(n) is 1.2–1.4 nm [56,57]. Although the structure of this study is different from TOPCon, it is instructive to note that simulations show that for TOPCon structures the fill-factor (FF) drops heavily for an oxide thickness exceeding ~ 1.6 nm [58]. In POLO-type SiO$_2$/poly-Si(n) passivating contacts, a thicker oxide of ~ 2.1 nm is used [59]. However, transport through such oxides is thought to mostly be aided by from pinholes in the oxide arising at high processing temperatures rather than tunneling [60]. In our case, the formation of such pinholes is deemed unlikely due to the very low processing temperatures. Nonetheless, the contact resistivity data of Fig. 5(b) shows that proper transport can take place across the relatively thick interfacial oxide formed between Nb$_2$O$_5$ and c-Si. Presumably, the substoichiometric nature of the interfacial oxide aids in transport [47].

At the moment, the exact role of the anneal which is applied after Al dot evaporation in improving the contact resistivity $\rho_c$ is not fully understood. Conceivably, the anneal leads to (i) a reduction in interface defect density, thereby (further) reducing Fermi level pinning; (ii) a change in the electron affinity of the ALD Nb$_2$O$_5$ as was observed by Hoffeditz et al. [51]; (iii) migration of oxygen from Nb$_2$O$_5$ to the adjacent interfaces, resulting in a more oxygen-deficient and conductive NbO$_x$ film. The oxygen potentially migrates to the Al capping layer...
termination of the contact resistivity has been indicated. In addition, for TiO2–C-Si/Nb2O5/Al. It should also be noted that the annealing conditions studies could help to further elucidate the exact nature of the interface Nb2O5 (i.e., no metallization) strongly grows upon annealing [47]. A thin SiO2 layer purposely grown by thermal oxidation was found to only provide improvements by using different annealing temperatures and times which induce an upward band bending of ~ 850 mV on 2.3 × 1017 cm−3-type (p-type) Si [5]. The fact that a low contact resistivity is obtained thus demonstrates that the upward band bending is at least partially negated by the contact formation. Although the origin and position of the fixed charge in AlNb2O5 is currently not known, it is conceivable that charged defect states play a role, which are annihilated or neutralized by changes in the Nb2O5 material properties upon contact deposition and subsequent annealing. It is also highly likely that the relatively low work function of the Al contact (~ 4 eV) contributes to a more downward band bending in the c-Si. Interestingly, a very similar result was found for ALD TiO2. Also for this material, part of the high level of passivation is attributed to the negative fixed charge in the material [16]. Nonetheless, proper electron-selective contacts have been produced with this material [17].

Although the thermal stability of Nb2O5-based contacts has not been thoroughly investigated yet, the higher crystallization temperature of Nb2O5 compared to TiO2 could be an advantage in this respect. For our Nb2O5 films, crystallization was found to occur at temperatures exceeding 550 °C, in line with literature values in the range of 500–700 °C [62–65]. TiO2 typically crystallizes at lower temperatures of 300–450 °C [66–68].

4. Conclusions and outlook

The presented results demonstrate that ALD Nb2O5 has interesting properties for passivating contact applications in terms of surface passivation, contact resistivity and optical transparency. ALD Nb2O5 can provide high levels of surface passivation, especially when deposited on a thin SiO2 interlayer. On such surfaces, J0 values down to 25 fA/cm² have been achieved. Moreover, the use of an SiO2 interlayer enables equally good passivation can be achieved using ultrathin Nb2O5 layers of 1 nm. On HF-treated surfaces, contact resistivity values as low as 0.070 Ωcm² have been demonstrated, showing the potential of using ALD Nb2O5 as full-area passivating contact. TEM imaging has elucidated that electrical transport takes place through a relatively thick interfacial oxide of (1.7 ± 0.2) nm, and it is thought that the sub-stoichiometric nature of this interfacial oxide aids in transport.

Future work can focus on verification of the charge carrier selectivity by evaluation of J0 after metallization and by application of ALD Nb2O5 in solar cell structures. Determining the contact resistivity of samples with a thin SiO2 layer is of high interest, as such substrates allow for excellent passivation using ultrathin 1–2 nm Nb2O5 films, potentially paving the way to an improved contact resistivity at similar or improved passivation levels. In addition, in analogy to the developments of the TiO2-based contact, the use of low work-function metal contacts such as Ca to induce downward band bending in the c-Si can be explored in a cell structure.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.solmat.2018.04.037.

References


