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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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ABSTRACT

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 $\sim$ 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 conductivity 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 $\sim$ 0.3Ωcm$^2$ 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], MgO [19], MoOx [20–22], WOx [23–25], V2Ox [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 J0 and ρ, 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-Si:H and poly-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 κ 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 antireflection coating in c-Si solar cells due 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 Qb 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 1–2×1012 cm−2. 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 ~ 4 eV [50]. Moreover, Hoffeditz 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 Nb2O5/c-Si interface exhibits a similarly small conduction band and large valence band offset as the TiOx/c-Si interface, which would facilitate selective electron transport. Indeed, in this work it will be shown that ALD Nb2O5 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 Nb2O5 as passivating contact material and outline directions for future improvements and further research.

2. Experimental section

Nb2O5 thin films were prepared by thermal atomic layer deposition (ALD) using (tert-butylimido)-tris(diethylamino)-niobium ((CH3)2CNi(N(C2H5)3)3, TBTDEN) as precursor and H2O 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. Post-deposition annealing treatments were carried out in a Jipelec rapid thermal anneal furnace at 300 °C in a forming gas ambient (10/90H2/Ar). This is attributed to a difference in injection-dependence of the lifetime. As can be seen in Fig. 5(b) of the Supplementary information, the lifetime on HF-treated substrates shows a slower decrease towards high-injection conditions. The obtained J0 values down to 25 fA/cm² are well-suited for passivating contact applications, although it should be noted that these have been evaluated prior to metallization. The combination of a high level of surface passivation and high transparency also makes the presented material interesting for application as a front floating emitter in n-type interdigitated back contacted (IBC) cells or as front surface field in p-type IBC cells.

In order to gain further insights into the passivating interface, the interface between ALD Nb2O5 and c-Si has been imaged by cross-sectional TEM. The visualized Nb2O5 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 Nb2O5 layer. As can be seen in Fig. 4, a (1.7 ± 0.2) nm interfacial SiO1.7 layer is formed. In previous work, X-ray photoelectron spectroscopy (XPS) studies showed that this SiOx layer mostly forms during post-deposition annealing of the sample at 300 °C and that this SiOx layer is strongly stoichiometric. Specifically, it is closer to SiO1.5 than it is to stoichiometric SiO2 [47].

In order to evaluate the contact resistivity ρc of ALD Nb2O5, 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 c-Si (n+) /Al. ALD Nb2O5 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 Nb2O5 films. Fig. 5(b) shows the extracted contact resistivity ρc values prior to annealing of the structure. Reasonably low contact resistivity ρc values of 0.10 and 0.21 Ω cm² 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 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 of ~ 4 eV. The proper contacting behavior observed when using Nb2O5 suggests that the Nb2O5 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 ρc values after annealing of samples with varying Nb2O5 film thickness are also shown in Fig. 5(b). The corresponding measured resistance values for the various Nb2O5 thicknesses as a function of the inverse dot diameter and the accompanying fits to the data used to extract the contact resistivity can be found in Fig. S3 of the Supplementary information. As can be clearly seen, the contact resistivity ρc values improve, and could now be determined for all the examined film thicknesses. A contact resistivity ρc of 0.070 Ω cm² is obtained for the 1 nm Nb2O5 film, whereas the 2 nm Nb2O5 film yields a slightly higher contact resistivity ρc of 0.124 Ω cm². These values are well in the relevant range of passivating contacts of ρc ≤ 0.3 Ω cm². 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 Ωcm). 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 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.
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.

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