Nickel Oxide Carrier Selective Contacts for Silicon Solar Cells

Raisul Islam, Pranav Ramesh, Ju Hyung Nam and Krishna C. Saraswat

Department of Electrical Engineering, Stanford University, Stanford, CA

Abstract — Highly selective contacts which allow one type of carrier (e.g., holes) to conduct and block the other type (e.g., electrons) are the key to achieving high efficiency is thin-film solar cells. Metal-insulator-semiconductor (MIS) carrier selective contacts can make a solar cell possible without a diffused p-n junction. In this work, we introduce nickel oxide (NiO) as a potential hole selective (electron blocking) contact on silicon. Using a metal/NiO/n-Si structure we have made a proof-of-concept device, which showed effective dark current suppression and photovoltaic power conversion when illuminated. We found that in the forward bias regime the injection current is suppressed due to the high conduction band offset between Si and NiO. This results in an improvement of $V_{oc}$ by 20 mV. The Si/NiO interface is limited by the defects but can be improved. The origin of these defects is the non-stoichiometry of NiO confirmed by X-ray photoemission spectroscopy. However, NiO is p-doped through non-stoichiometry, which is important for hole selectivity. Therefore, NiO stoichiometry is proposed to be the design optimization parameter in metal/NiO/Si selective contacts.

I. INTRODUCTION

Traditional solar cell structures make use of p-n junctions to separate photogenerated carriers by behaving as selective contacts due to the built-in potential. However, they provide poor selectivity due to back-injection over the barrier. In addition, the high temperature processing required for dopant diffusion during junction formation results in the degradation of the semiconductor bulk properties. It has been stated that significantly improved contact selectivity is necessary for achieving quantum efficiencies higher than 25% [1].

Contacts using metal-insulator-semiconductor (MIS) structures have been investigated for improved carrier selectivity since the 1970’s [2]. An insulator is inserted between metal and semiconductor to block the flow of either electrons or holes across the junction. However, the insulators employed in these schemes reduced both electron and hole current by introducing large barriers for both types of carriers, greatly degrading solar cell performance. Recently, using MIS structures, a solar cell employing double heterojunction has been proposed which does not require any p-n homojunction [3, 4].

It has been shown that junctions with a large barrier for one type of carrier but a small barrier for the other are necessary to provide proper selectivity in this MIS scheme. Materials with the proper band lineup must be chosen to create both electron and hole selective contacts. TiO$_2$ is one such material that has been used to create effective electron selective (hole blocking) contacts to Si due to its low conduction band offset and high valence band offset [4].

Creating hole selective contacts, however, has been more difficult. PEDOT:PSS has been implemented as a hole selective contact on Si [4] but suffers from long-term stability issues due to being an organic material. The use of an inorganic material provides benefits in terms of stability as well as process compatibility.

We propose nickel oxide as an inorganic interfacial layer for hole selective contacts on Si. Fig. 1 shows the band lineup of a metal/NiO/Si junction. The large conduction band offset between NiO and Si introduces an energy barrier to block electron current while the small valence band offset still allows the flow of holes through the junction.

![Fig. 1. Band lineup of metal/NiO/Si junction. The band diagram demonstrates the concept of hole selective contacts.](image)

In this work, we demonstrate NiO to be a good hole selective contact with our proof-of-concept device. The dark current is suppressed by one order of magnitude when NiO is inserted between metal and silicon. In addition there is minimal degradation of light induced current, an indication of good selectivity.

We also find that the NiO/Si interface needs to be optimized to further improve the performance of the device. Material characterization indicates oxide stoichiometry as one possible reason for the defective interface. Altering the oxygen content in the film may result in better surface passivation. However, lowering the oxygen content results in high resistivity, thereby degrading selectivity. Further work is being pursued using annealing and additional passivation layers to investigate the tradeoff between interface quality and contact selectivity.

II. EXPERIMENTAL DESCRIPTION

Silicon wafers doped to $10^{15}$ cm$^{-3}$ n-type were used for device fabrication. First, 20 nm Al$_2$O$_3$ was deposited using ALD. This layer serves as a passivation to prevent any lateral
current spreading. 2 µmx 4 µm windows were patterned and the alumina was etched for NiO deposition. 2 nm of amorphous NiO (RMS surface roughness of 0.305 nm) was then deposited using a magnetron sputtering system with a NiO target. The RF power was set to 150 W and the chamber pressure was 3 mTorr. The O:Ar ratio was maintained at 1:9. Following the NiO growth, a 50 nm platinum anode was deposited in situ. Finally, both the NiO and Pt contacts were patterned using liftoff. The structure of the device is shown in Fig. 2.

**Fig. 2.** Schematic of the device structure. Control sample is composed of similar structure without the NiO layer.

**III. RESULTS AND DISCUSSION**

A. NiO as a Selective Contact

In this section, we present the proof-of-concept of the hole selective contact (an electron blocking layer) with respect to silicon using nickel oxide. The open circuit voltage, \( V_{oc} \), increases when the short circuit current is increased and dark current is suppressed. Short circuit current is limited by photon absorption, carrier generation, and collection.

Therefore, in order to improve \( V_{oc} \), the dark current must be minimized. Fig. 3 shows the dark current of the fabricated device both with and without NiO. Without NiO, the device exhibits higher dark current than that with NiO. When 2 nm NiO is inserted between the metal and the semiconductor, the forward bias current is reduced by one order of magnitude. At forward bias, the injection of electrons from the semiconductor to the anode reduces significantly due to the high conduction band offset between NiO and Si, which results in a large drop in current. In the diffusion region of the forward bias current (0.5 V – 1 V), the ideality factor (n) slightly increases with the insertion of NiO. This increase can be attributed to SRH recombination of hole injected from the anode at forward bias with electrons blocked at Si/NiO interface. However, this also signifies that the injection current from n-Si to the anode decreases significantly. Since the SRH recombination (n = 2) has a weaker voltage dependence than injection current (n = 1), better \( V_{oc} \) can be observed from this device.

We also show the light induced current in Fig. 3. Note that in order to obtain the light I-V characteristics we used a 150 W halogen lamp, which does not correspond to the I-V relationship obtained using standard illumination conditions. However, this method is sufficient to prove NiO functions as a hole selective contact. The device fabrication and metal contact dimensions are not optimized for a standard solar cell, so the light I-V curve cannot be used to benchmark the proposed device against other solar cell structures.

The light I-V shows a 20 mV improvement in \( V_{oc} \) proving the advantage of using a high barrier offset to block electrons and thereby lower the dark current. However, there are two requirements for a hole selective contact. One is to block electron current and the other is to allow hole current. From the light I-V, we can see that the current level does not degrade significantly when NiO is inserted between metal and Si. This means that although NiO blocks electrons, it allows holes and therefore the metal/NiO/n-Si structure can be used as a photovoltaic device.
B. Recombination Characteristics

In the previous subsection, we have mentioned that the ideality factor in the forward bias region increases for the metal/NiO/Si structure. That means the reverse bias current should be dependent on temperature. We present the dark I-V for three different temperatures in Fig. 4(a). The reverse saturation current $i_0$ is extracted and plotted in Fig. 4(b) as a function of $1/T$. The dependence of $\ln(i_0/T^2)$ on $1/T$ is linear. The activation energy of recombination is extracted to be 0.42 eV, which is very close to the midgap value of Si, confirming the SRH nature of the recombination.

C. Interface Characterization

Dangling bonds create interface defect states, which reduce the open circuit voltage and are detrimental to the efficiency of the cell. In order to characterize the NiO/Si interface double-sided polished CZ silicon wafers doped to $10^{15}$ cm$^{-3}$ n-type were used. At first, high quality thermal SiO$_2$ was grown by dry oxidation at 1100°C. The thermal oxide on the top surface was etched and 10 nm NiO was sputtered on the Si surface. Thermal SiO$_2$ is known to provide high quality passivation, resulting in low defect density on the backside of the sample. Therefore the interface passivation will be limited by the quality of the Si/NiO interface.

Minority carrier lifetime measurements were performed to characterize the interface quality. A Semilab $\mu$-PCD measurement tool was used to do the lifetime measurements. Excluding the wafer edges, the average measured lifetime is 61.54 µs. The lifetime of a SiO$_2$/Si/SiO$_2$ structure is measured to be 365 µs using the same technique. The lifetime with NiO on Si is lower than what is obtained from SiO$_2$ passivation. One possible reason for this decrease in lifetime is non-stoichiometry, which not only adds interface defect states but also creates defect states within NiO. These states act as electron hopping paths through NiO, defeating the purpose of using it as a selective contact. Non-stoichiometry of the NiO is confirmed by X-ray photoemission spectroscopy (XPS) (Fig. 5). In this figure, we can see that the defect state (Ni$^{3+}$) in both O 1s and Ni 2p 3/2 elemental scan is prominent. Using O 1s scan by fitting the peaks with Gaussian curves and comparing the area under the two peaks, the ratio between O and Ni is calculated to be 1.2748. The as deposited NiO is oxygen rich, which usually behaves as a p-type semiconductor [5]. This means there is a tradeoff in how much NiO can be made stoichiometric before the other parameters start to suffer. However, the reduction in defects can be possible with annealing or using another passivation layer in between. Both of these paths are currently being pursued.

IV. CONCLUSION

We have demonstrated a hole selective contact using NiO as an insulator between metal and silicon. A single MIS solar cell using NiO can provide 20 mV of open circuit voltage gain. The dark current is suppressed by one order of magnitude. However, the overall lifetime degrades with NiO deposition on Si. XPS shows that the as deposited NiO is non-stoichiometric. Making it more stoichiometric by annealing would improve the lifetime and hence increase the electron blocking property of the selective contact. However, making NiO more stoichiometric would decrease the conductivity since NiO is doped by oxygen defects. This results in a tradeoff between making the NiO more stoichiometric and keeping it conductive through defect doping. Proper design optimization is the key to achieve high efficiency from the photovoltaic cells using NiO selective contacts.

REFERENCES


