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Transmission Electron Microscopy Studies of Transition Metal Oxides Employed as Carrier Selective Contacts in Silicon Solar Cells

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Abstract — The focus of this work is on the nano-scale characterization of transition metal oxides employed as carrier selective contacts in silicon solar cells using cross-sectional transmission electron microscopy (TEM). Both electron-selective (titanium oxide, TiO_2) and hole-selective (molybdenum oxide, MoO_x; tungsten oxide, WO_x) contacts were investigated. Bright-field (BF) as well as high-resolution TEM (HRTEM) micrographs were obtained with a FEI Tecnai F30 TEM.

I. Introduction

Silicon solar cells have recently been able to exceed the 25% efficiency mark using carrier selective contacts. These contact stacks not only passivate the silicon surface but are also carrier-selective, meaning they allow only one type of carrier, i.e., either electron or hole to pass through. Traditionally, carrier selective contacts to silicon solar cells have been realized by using intrinsic hydrogenated amorphous silicon a-Si:H(i) as a passivation layer in combination with either an a-Si:H(n) or a-Si:H(p) film to make the contact electron selective or a hole selective contact respectively. In some cases, very thin (1-2 nm) silicon oxide (SiO_x) films have also been used as a passivation layer in combination with a-Si:H(n/p) or with doped polycrystalline silicon. However, these cells have certain inherent drawbacks associated with them such as thermal instability (for a-Si:H), parasitic photon absorption, complicated deposition processes and high fabrication costs.[1, 2]

To overcome these limitations, transition metal oxides have been extensively explored as an alternative to a-Si:H(n/p) for use as carrier selective contacts in silicon solar cells. These carrier selective contacts typically consist of a thin (<10 nm) metal oxide film. Electron or hole selectivity is dictated by the work function, band gap, and band offsets of the metal oxide used compared to the Si absorber. For instance, titanium oxide (TiO_2) has a small conduction band offset (ΔE_c = 0.05 eV), which allows electrons to pass through the TiO_2 layer, and a large valence-band offset (ΔE_v = 2.0 eV) that blocks holes. As a result, TiO_2 has been extensively studied as an electron-selective rear contact for n-type cells.[3, 4] For hole selective contacts, high work function metal oxides have been used. The strong work function difference between the Si and metal oxide induces a strong upward band bending at the Si surface, resulting in an accumulation of holes and depletion of electrons. sub-stochiometric MoO_x and WO_x have been demonstrated to be effective hole selective front contacts for n-type cells.[5, 6]

Although silicon solar cells featuring transition metal oxide based carrier selective contacts have achieved reasonably high efficiencies, there is still room for improvement. These carrier selective contacts still suffer from certain drawbacks. For instance, although MoO_x and WO_x have emerged as promising materials for hole selective front contacts in n-type silicon solar cells, their optical and electrical properties are susceptible to degradation when subjected to low temperature anneal.[7] Therefore, to achieve cell

efficiencies approaching the theoretical limit, it is essential that the underlying mechanisms of these carrier selective contacts are fully understood. The objective of this paper is to demonstrate how nano-scale characterization of carrier selective contacts using transmission electron microscopy (TEM) can be used to gain fundamental insight into passivated contact stacks. Both electron-selective (TiO_2) and hole-selective (MoO_x, WO_x) contacts were investigated in this study.

II. EXPERIMENTAL

TiO_2 films (<5 nm) were deposited by atomic layer deposition (ALD) on {100} *n*-type Si wafers. For the ALD process, $TiCl_4$ was used as the Ti precursor, H_2O as the oxidant, N_2 as the purge gas, and deposition temperature used was 75°C. Prior to deposition of TiO_2, the wafers were chemically polished and Radio Corporation of America cleaned followed by a short dip in dilute hydrofluoric acid. Then, samples were subject to thermal oxidation in a preheated quartz tube furnace at 700°C to allow a thin SiO_2 (<2 nm) layer to grow. Finally, Al contacts (~2 μm) were formed over TiO_2 layer by thermal evaporation.

MoO_x and WO_x thin films (<10 nm) were deposited on {100} *p*-type Si wafers under vacuum by thermal evaporation using a solid MoO_3 and WO_3 source respectively. During the evaporation process, heating of the Si substrate was negligible and remained at ambient temperature. Then, 50 nm thick transparent conducting oxide (TCO) layer of indium tin oxide (ITO) was deposited by RF-magnetron sputtering in an Ar atmosphere at room temperature. Select samples were then annealed in air at 200°C for 30 min.

Contact resistivity measurements for both pre- and post-annealed samples were carried out by transmission line measurement (TLM) technique. TLM was used to measure the lumped contact resistivity of each passivated contact structure. A Keithley 2400 Sourcemeter was used to collect the electrical data of these samples. Silver (Ag) metal contacts were thermally evaporated through a shadow mask to create the TLM patterns for these samples.

For TEM studies, cross-sectional TEM specimens were prepared by focused ion beam (FIB) milling technique and with the help of FEI 200 TEM FIB. Specimen lift-out was done in-situ and attached to Cu gird. TEM studies were performed with the help of FEI Tecnai F 30 TEM under operating voltage of 300 KV. Cross-sectional micrographs were obtained under bright field (BF) and high-resolution transmission electron microscopy (HRTEM) conditions with a point-to-point resolution of 0.2 nm.
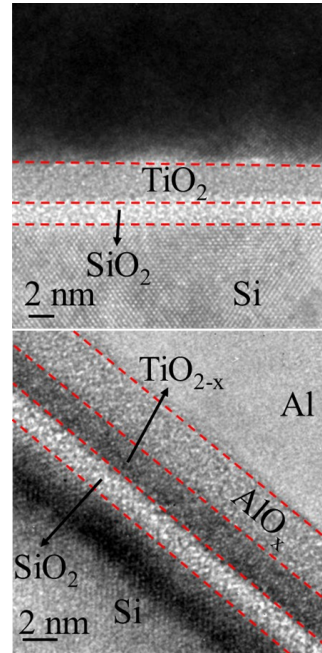
III. RESULTS AND DISCUSSION

Fig. 1. HRTEM images of $Si/SiO_2/TiO_2$ (left), after Al deposition (right).

It is evident from Figure 1 that when Al is deposited over the thin TiO_2, an interlayer of AlO_x is formed at the TiO_2/Al interface. This occurs because of diffusion of oxygen from TiO_2 towards Al, which is due to the higher oxygen affinity of the Al as compared to that of the Ti. Consequently, TiO_2 is reduced to oxygen-deficient TiO_{2-x} containing large number of oxygen vacancies which increases its conductivity but is expected to degrade its passivation behavior. This has been previously reported by Yang *et al.* and Ali *et al.* [3, 4]

Table 1: Contact resistivity values obtained from TLM measurements for the hole selective MoO_x and WO_x contacts.

Contact structure	Contact resistivity ($m\Omega.cm^2$)	
	No anneal	Annealed
MoO_x/ITO/Ag	80	290
WO_x/ITO/Ag	95	122

The contact resistivity of MoO_x/ITO/Ag and WO_x/ITO/Ag structures were measured both before and after annealing by TLM technique and the measured values are listed in Table 1. It is evident that contact resistivity increases upon annealing although the increase in contact resistivity is much more pronounced for MoO_x/ITO/Ag contact structure. To investigate this further, TEM studies were carried out for both the contact structures.
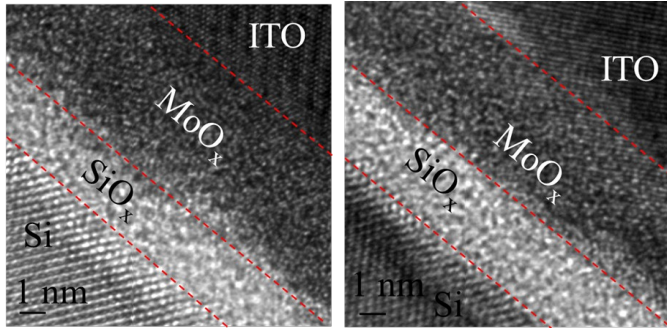

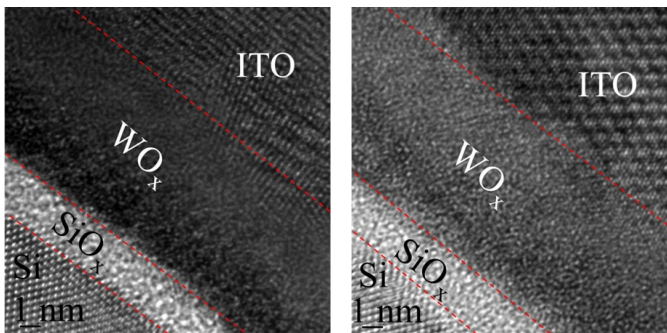Fig. 2. HRTEM images of Si/MoO_x/ITO: as-deposited (left), after annealing (right).

Fig. 3. HRTEM images of Si/WO_x/ITO: as-deposited (left), after annealing (right).

It was observed in HRTEM images that a SiO_x interlayer having thicknesses in the range of 2-3 nm and 1-2 nm was present at Si/MoO_x and Si/WO_x interfaces respectively, even for pre-annealed samples. Furthermore, no apparent change in the SiO_x interlayer chemistry was observed, even after annealing in both contact structures. Typical HRTEM images of pre- and post-annealed Si/MoO_x/ITO and Si/WO_x/ITO

contact structures are shown in Fig 2. and Fig 3. respectively. It has been previously proposed that increase in contact resistivity upon annealing is likely due to formation of hole-blocking interlayer at MoO_x/ITO interface[8]. However, no such interlayer was observed at either MoO_x/ITO or WO_x/ITO interfaces.

Overall, it appears that the increase in contact resistivity for Si/MoO_x/ITO and Si/WO_x/ITO contact structures is likely to due to subtle changes occurring either within the MoO_x, WO_x layers or at the SiO_x/MoO_x, SiO_x/WO_x interfaces. This requires further investigation with the help of advanced analytical TEM techniques including electron energy loss spectroscopy (EELS) in combination with energy loss near-edge structure (ELNES) and extended energy-loss fine structure (EXELFS).

IV. CONCLUSION

In summary, this work has provided valuable information about stability of transition metal oxide based carrier selective contacts employed in silicon solar cells. It has been demonstrated that TEM studies can be very useful for understanding the behavior of these carrier selective contacts at the nano-scale. HRTEM imaging in combination with analytical TEM techniques can be employed to detect the formation of interlayers at various interfaces as well as any chemical changes and elemental diffusion (e.g., oxygen diffusion) within the contact structures.

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