



Oxygen vacancies in tungsten oxide and their influence on tungsten oxide/silicon heterojunction solar cells



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ABSTRACT

Tungsten oxide (WO_x) can be incorporated into amorphous/crystalline silicon heterojunction solar cells as hole contact and for interface modification between p-type amorphous silicon and indium tin oxide. This paper aims at understanding the influence of tungsten oxides properties on silicon heterojunction solar cells. Using in-system photoelectron spectroscopy on thermally evaporated WO_x layers, it was verified that WO_x with a stoichiometry close to WO_3 features a work function close to 6 eV and is therefore suitable as hole contact on silicon. Additionally the oxygen vacancy concentration in WO_x was measured using photoelectron spectroscopy. High oxygen vacancy concentrations in WO_x lead to a low band bending in the WO_x /silicon-junction. Furthermore solar cells were fabricated using the same WO_x , and the band bending in these cells is correlated with their fill factors (FF) and open circuit voltages (V_{OC}). Combining these results, the following picture arises: positively charged oxygen vacancies raise the Fermi-level in WO_x and reduce the band bending at the WO_x /silicon-junction. This, in turn, leads to reduced V_{OC} and FF. Thus, when incorporating WO_x into silicon solar cells it is important to minimize the oxygen vacancy density in WO_x . Therefore deposition methods, enabling adjustment of the WO_x stoichiometry are preferable.

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1. Introduction

Amorphous/crystalline silicon heterojunction solar cells have enabled the highest efficiency of all silicon wafer based solar cells [1]. The main advantage of silicon heterojunction solar cells is their excellent contact passivation by intrinsic amorphous silicon ((i)a-Si:H), which enabled open circuit voltages (V_{OC}) of up to 750 meV [2].

Recently researchers focused on the carrier transport across the indium-tin-oxide (ITO)/p-type amorphous silicon ((p)a-Si:H) junction [3,4]. During this studies it was found that the low work function of indium-tin-oxide [4] and aluminum doped zinc oxide [5,6] limits the carrier transport across the interface between the transparent conductive oxide and the p-type amorphous silicon [4,5].

This has incited a number of works on different high work function metal oxides like molybdenum oxide [7], tungsten oxide [8] and vanadium oxide [9] as hole contacts on silicon solar cells, or for band alignment adjustment at the TCO/(p)a-Si:H-junction [4]. Recently interest has shifted towards the direct application of high work function metal oxides as hole contacts on (i)a-Si:H

passivation layers [8,10], which already yielded 22.5% efficiency for molybdenum oxide hole contacts [11], with a conventional (n)a-Si:H electron contact. One advantage of this approach is the lower parasitic absorption in metal oxides as compared to doped amorphous silicon contacts [10].

Also low work function materials were applied as electron contacts leading to 20.5% efficiency for TiO_x [12] with a diffused hole contact, 14% efficiency for Cs_2CO_3 with a PEDOT:pss hole contact [13] and 19.4% efficiency with a lithium fluoride electron contact and a molybdenum oxide hole contact deposited on (i)a-Si:H passivation layers [14].

Molybdenum oxide has been widely applied as a hole collection layer in organic solar cells [15,16] and later transferred to silicon based devices to fulfill the same function. Multiple studies found that molybdenum oxide contacts on silicon degrade under annealing at 200 °C [8,11] and atomic layer deposition of molybdenum oxide at higher temperature was also found to yield low quality contacts [17,18]. Therefore silicon heterojunction solar cells with molybdenum oxide contacts degrade significantly during curing of common silver pastes [11].

In contrast tungsten oxide, which was also applied as hole collection layer in organic solar cells [15,16], is stable during annealing at 200 °C [8] and yields better fill factors than molybdenum oxide, when applied for interface modification at the TCO/(p)a-Si:H interface [8]. Unfortunately tungsten oxide hole contact

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layers deposited directly on (i)a-Si:H passivation layers [8], or n-type crystalline silicon [9] only yield comparatively low fill factors and limited open circuit voltages.

The present article studies WO_x as an interlayer, or hole contact in SHJ solar cells and investigates the influence of its chemical structure on solar cell properties. The reason for the low performance of thermally evaporated tungsten oxide hole contacts on silicon is identified and a way to improve the material is proposed.

2. Materials and methods

2.1. Preparation of tungsten oxide

Tungsten oxide was deposited by thermal evaporation at 920 °C from a tungsten crucible onto a substrate kept at ambient temperature. The depositions were conducted in an ultrahigh vacuum system with a base pressure of 1×10^{-9} mbar. The substrates were either crystalline silicon wafers, or nominally identical wafers covered by 6 nm intrinsic amorphous silicon. These substrates were dipped in diluted hydrofluoric acid (1%, 1 min) before they were transferred into the ultra high vacuum system. The source material was tungsten oxide (WO_3) powder with a purity of 99.99% from Alfa Aesar. The deposition rate was varied from 0.3 to 2 nm/min to attain different stoichiometry and oxygen vacancy concentrations in these layers.

Selected layers were exposed to oxygen plasma treatments in the same chamber at an oxygen pressure of 1×10^{-5} mbar for 10 min. These layers were neither included in solar cells, nor used for work function measurements. Instead they were only used to attain x-ray photoelectron spectra of near stoichiometric layers.

2.2. Solar cell process

Single 1×1 cm solar cells were prepared on 3×3 cm pieces of 280 μ m thick, polished phosphorous doped float-zone grown c-Si wafers with (111) surface orientation and a resistivity of 3 Ω cm. Wafers were cleaned using the RCA process and dipped in diluted hydrofluoric acid (1%, 2 min) before layer deposition. Then intrinsic a-Si:H passivation layers were deposited using plasma enhanced chemical vapor deposition with 13.56 MHz excitation, a process pressure of 0.5 mbar, a substrate temperature of 170 °C, an electrode distance of 3 cm, a plasma power density of 19 mW/cm², and a silane flow of 10 sccm. Afterwards the layers were exposed to a hydrogen plasma treatment step to decrease the interface defect density at the silicon heterojunction [19]. The plasma parameters were 1 mbar process pressure, a power density of 56 mW/cm², a substrate temperature of 170 °C, an electrode distance of 5 cm and a hydrogen flow rate of 20 sccm. For solar cell fabrication wafers were coated with 4 nm intrinsic a-Si:H and 8 nm n-type a-Si:H on the backside and 5 nm intrinsic a-Si:H and tungsten oxide layers with thicknesses of 5–30 nm on the front side. These WO_x layers were also prepared in the ultra high vacuum system. Reference solar cells were coated with 8 nm p-type a-Si:H instead of tungsten oxide on the front side. The solar cells were then completed by ITO sputtering at room temperature and from a ceramic target. Afterwards the samples were annealed for 5 min at 200 °C and metalized with Ti/Ag stacks. The full solar cell process is discussed elsewhere [20].

2.3. Photoelectron spectroscopy

All photoelectron spectroscopy measurements were conducted in the same UHV system as the tungsten oxide evaporation. The chamber for photoelectron spectroscopy measurements is

connected to the evaporation chamber, but the connection is interrupted during depositions and measurements. The base pressure is 1×10^{-9} mbar. He-UPS measurements with an excitation energy of 21.2 eV were conducted directly after the depositions (maximum 20 min between deposition and measurement), since He-UPS is very surface sensitive and contaminations such as adsorbates from the residual gas could influence the work function of the samples. The work function was determined by fitting a Boltzmann sigmoid function to the secondary electron cut-off.

X-ray photoelectron spectroscopy was applied to obtain the stoichiometry of tungsten oxide layers. The tungsten 4f core level was measured and fitted according to the analysis presented by Bussolotti et al. [21] and adjusted by other groups [22,23]. According to this interpretation the 4f orbital signal of tungsten consists of a doublet of the 7/2 and 5/2 spin states with an energy shift of 2.12 eV between the two components of the doublet, an intensity ratio of 0.75 and the same full width at half maximum for both peaks.

Each doublet consists of three signals. One is the signal of W^{6+} , which has a binding energy of about 35.9 eV for the 7/2 spin state. This is stoichiometric tungsten trioxide (WO_3). The second signal is W^{5+} (W_2O_5) and its binding energy was kept as a fixed energy distance of 1.2 eV lower than the one of W^{6+} . Finally the third signal is located 0.5 eV above the binding energy of W^{6+} and is related to the barrier height inhomogeneity (BHI) [24] induced by oxygen vacancy defects at the tungsten oxide surface. Note that the signal of the BHI is purely surface related and absent from samples measured with atmospheric contaminations like adventitious carbon [25]. Therefore in-system measurements without a vacuum break are instrumental for an analysis of this property.

Fitting of the data with only one, or two signals per doublet was done, but three signals and especially a signal with a binding energy of about 0.5–0.6 eV above the binding energy of W^{6+} are needed to attain good fits to the data.

All in all this fit model has seven fitting parameters, being the binding energy of the W^{6+} 7/2 spin state, which also determines all other binding energies, and the three intensities and three full widths at half maximum of the three signals.

2.4. Other measurements and numerical device simulation

Surface photo voltage measurements with 905 nm laser excitation [26] were used to measure the band bending in samples with tungsten oxide on n-type crystalline silicon, or n-type crystalline silicon with intrinsic amorphous silicon passivation layers and in finished solar cells. The passivated back side of the finished solar cells increases the decay time of the voltage pulse, since recombination at this interface is suppressed. This is of no consequence to the measured value of the voltage pulse. Additionally the n-doped layer on the back-side fixes the Fermi-level at the back-side and provides a defined back contact. Therefore surface photo voltage measurements on finished solar cells should be less variable than on samples with unprocessed back-sides.

Solar cell measurements were conducted using a solar simulator with class AAA AM1.5GMM illumination at 25 °C. The numerical device simulator AFORS-HET [27] was used to simulate the carrier extraction from a crystalline silicon absorber using different contact systems. The simulation model consisted of 250 μ m thick n-type crystalline silicon symmetrically passivated by 5 nm intrinsic hydrogenated amorphous silicon. The a-Si:H layers were simulated using an electron affinity of 3.724 eV and a band gap of 1.68 eV. The charge selective contacts were implemented by defining two Schottky-contacts with a recombination velocity of 1 cm/s for one carrier type effectively blocking the extraction of

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