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# *n*- and *p*-type silicon solar cells with molybdenum oxide hole contacts

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### **Abstract**

This paper provides an experimental proof-of-concept for simple solar cell designs on n- and p-type crystalline silicon (*c*-Si) substrates which utilise sub-stoichiometric MoO<sub>x</sub> ( $x < 3$ ) films to collect holes. The n-type cell design (referred to as 'molypoly') features a planar rear  $SiO_x / poly-Si(n^+)$  stack with a planar front  $SiO_x / MOO_x / ITO$  stack. We demonstrate an unoptimised conversion efficiency of  $\sim 16.7 \pm 1\%$  for a 3 x 3cm cell using a simple 10-step fabrication procedure. The p-type cell design (referred to as 'moly-BSR') is comprised of a simple  $\text{SiN}_x$  passivated, textured, front phosphorus diffusion with a rear  $MO_{x}$  / Ag hole contact. A conversion efficiency of  $\sim 16.4\pm 1\%$  is achieved for 2 x 2cm using an 11-step fabrication procedure. Beyond the proof-of-concept results achieved, a number of future improvements are also outlined.

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# **1. Introduction**

A central premise of a photovoltaic device is the separation of photo-excited electrons and holes at opposite contacts. The present paper focuses specifically on the anode, or hole collecting contact of crystalline silicon (c-Si) solar cells. Table 1 compares the best cell-level results for a wide variety of c-Si solar cells featuring different types of full-area hole contacts. The top three entry types all utilize  $p^+$  doped silicon layers to collect holes. These structures have received considerably more attention from the silicon photovoltaic community and have demonstrated much higher device efficiencies, assisted, at least in part, by knowledge inherited from the silicon microelectronics industry. However, these contact types are still limited by issues such as parasitic absorption, fundamental recombination losses and high temperature processing. This has prompted continued research into alternative hole contacting structures.

The lower half of the table reflects less explored cell structures which utilize non-silicon based materials to promote hole collection. Amongst these, structures utilizing sub-stoichiometric molybdenum oxide MoOx, offer the additional benefits of ease of fabrication and favorable optical properties for photovoltaic applications. The very high work function of MoO<sub>x</sub> has proven beneficial in the collection of holes on a number of solar cell absorber materials and has only recently been transferred to c-Si [1-3], with measured contact resistivities on the order of 1  $m\Omega$  cm<sup>2</sup> for moderate silicon doping [3]. It has also been recently demonstrated that when thermally evaporated in a controlled manner this film can provide surface passivation to c-Si with corresponding recombination parameters  $J_0$ between 200 and 300 fA/cm<sup>2</sup> [3]. If these values can be effectively transferred to solar cell designs then MoO<sub>x</sub> hole contacts will offer significant gains over conventional approaches in terms of recombination, thermal budget and simplicity. This paper explores the use of full area  $MoO<sub>x</sub>$  contacts to collect holes on simple n- and p-type c-Si solar cells.

Full area hole contact type	Hole contact structure	Holes in the absorber	$V_{\rm oc}$ (mV)	FF(%)	$\eta$ (%)	Ref.
Aluminum alloyed homojunction	c-Si $(p)$ / c-Si(Al- $p^+$ )	Majority	648	80.6	20.1	$[4]$
Amorphous silicon heterojunction	c-Si $(n)$ /a-Si:H(i) / a-Si:H(p <sup>+</sup> ) / TCO <sup>*</sup>	Minority	750	83.2	24.7	[5]
Semiconductor-insulator- semiconductor	c-Si $(n)$ / SiO <sub>x</sub> / poly-Si $(p^+)$ / Ag	Minority	693	81.5	17.9	[6]
	c-Si $(n)$ / SiO <sub>x</sub> / a-Si:H $(p^+)$ <sup>*</sup>	Minority	739	80.45	23.12	$[7]$
Metal-insulator-semiconductor	c-Si $(n)/$ SiO <sub>x</sub> / Au	Minority	550	72	9	[8]
Silicon / organic hybrid	$c-Si(n)$ / PEDOT:PSS	Minority	653	67.2	17.4	[9]
Silicon / carbon nanotube	$c-Si(n)$ / carbon nanotube	Minority	530	74.1	11.2	[10]
Silicon / graphene	$c-Si(n)$ / Graphene	Minority	552	48	10.3	[11]
Silicon / metal oxide	$c-Si(n)/MO_x$	Minority	580	65	14.3	$\lceil 1 \rceil$
	$c-Si(n) / a-Si:H(i) / MOx$	Minority	711	67.2	18.8	$[2]$
Silicon / metal oxide	$c-Si(n)/MO_x$	<b>Minority</b>	637	75	16.7	T.W.
	$c-Si(p) / MoOx$	Majority	616	72	16.4	T.W.

Table 1. Comparison of open circuit voltage  $(V_{\text{oc}})$ , fill factor (FF) and efficiency  $(\eta)$  for a variety of full-area hole contacts implemented in c-Si solar cells. (T.W. denotes this work.)

*\* The exact structures of these cells are not known* 

#### **2. Device structure and fabrication**

Figure 1 shows the structure and fabrication procedure for the n- and p-type cells utilizing  $MoO<sub>x</sub>$  hole contacts. The n-type cells (referred to henceforth as the 'moly-poly' cells) were fabricated using planar,  $\sim$ 1  $\Omega$ cm, FZ, 250  $\mu$ m, n-type wafers. A thick  $SiO<sub>x</sub>$  layer was grown on the surfaces, via wet oxidation, to act as a protective mask in subsequent steps. This oxide was removed from the rear-side of the wafer using HF fuming and an  $SiO<sub>x</sub>$  / poly-Si (n<sup>+</sup> ) stack was deposited to form the rear electron contact, as described in ref. [4]. Following this step the front oxide was removed using dilute HF. The cells were then cleaned using a standard RCA procedure; the thin oxide formed during this process was intentionally left on. A MoO<sub>x</sub> (~15 nm) / indium-tin-oxide (ITO, ~50 nm) stack was then deposited on top of the thin chemical oxide layer. The  $MoO<sub>x</sub>$  was deposited by thermal evaporation (Angstrom Engineering ÅMOD) from a high purity powder source at a rate of  $\sim$ 1 Å/sec using a base pressure of  $\lt 7x10^{-7}$ mTorr. The ITO was deposited via RF sputtering (AJA International, ATC Orion) and had a sheet resistance of  $\sim$ 120  $\Omega/\square$ . A silver fingered grid (~10% contact area) and a silver full area contact were then deposited via thermal evaporation on the front and the rear of the cell, respectively. Finally, the cell area was defined by laser cutting; no attempt was made to reduce the effects of laser induced edge recombination in these proof-of-concept cells.

The p-type cells (referred to henceforth as 'moly-BSR') were fabricated on planar,  $\sim$ 2  $\Omega$ cm, FZ, 250  $\mu$ m, p-type wafers. Following wet oxidation, the front oxide was removed via HF fuming and the exposed surface was textured using an alkaline based etch solution. After an RCA cleaning step, a heavy phosphorus diffusion (~20  $\Omega/\square$ ) was performed. An Al metal grid  $(\sim 10\%$  metal fraction) was then evaporated on the front-side and the diffusion was etched back to ~100  $\Omega/\square$  in the non-metalized regions, as described in ref [5]. A ~75 nm SiN<sub>x</sub> passivation and antireflection coating was then deposited via plasma enhanced chemical vapor deposition (PECVD, Roth and Rau AK 400). The rear protective oxide was removed by HF fuming and a MoO<sub>x</sub> (15 nm) / Ag (2  $\mu$ m) stack was deposited by thermal evaporation (for both the  $Mo_{x}$  and Ag layers). Both the moly-poly and moly-BSR cells utilize a coarse front metal grid formed by thermal evaporation through a shadow mask; hence no photolithography steps were used in the fabrication procedure.

Illuminated IV cell characteristics were measured under standard 1-sun conditions (~1000 W/m<sup>2</sup>, ~25 °C, AM 1.5 G spectrum) using a solar simulator (Photo Emission Tech, model SS150) which was calibrated using a certified reference cell from Fraunhofer ISE CalLab. We estimate and absolute efficiency uncertainty of  $\pm$  1%.



moly - poly

10.) Rear Ag evaporation



molv BSR

- 1.) Thick wet oxidation
- 2.) Front oxide removal (HF)
- 3.) Front side texturing
- 4.) Phosphorus diffusion
- 5.) HF / RCA Cleaning
- 6.) Front shadow AI evaporation
- 7.) Alkaline etch-back
- 8.) Front SiNx (PECVD)
- 9.) Rear oxide removal (HF)
- 10.) MoOx evaporation
- 11.) Rear Ag evaporation

Fig 1 – Representative schematic of the proof-of-concept moly-poly and moly-BSR cell architectures. The major fabrication steps are listed below the schematics

# **3. Device characterization**

Figure 2 a and b provide representative light IV characteristics (open circuit voltage  $V_{\text{oc}}$ , short circuit current  $J_{\text{sc}}$ , fill factor *FF* and efficiency  $\eta$ ) for the moly-poly and moly-BSR cells, respectively. For the moly-poly cell a  $V_{\text{oc}}$  of 637 mV is slightly higher than typical values for industrial screen printed  $AI-p^+$  solar cells. The main losses stem from the low current density (due to the planar front surface and coarse front metal grid) and fill factor (also partly attributable to the thin metal of the front grid). It is envisioned that a significant increase in current density (up to  $\sim$ 4 mA/cm<sup>2</sup>) could be achieved by using a finer front metal grid and surface texturing. In addition, the insertion of an

The  $V_{\text{oc}}$  of the moly-BSR cells is significantly lower, at ~616 mV, whereas  $J_{\text{sc}}$  is higher, courtesy of the front surface texturing. This device did not have the thin chemical SiOx layer present in the moly-poly cell, but even without it a recombination current density of  $\sim 200$  fA/cm<sup>2</sup> is expected as inferred from previous studies on simplified test structures [3]. Unfortunately, as can be seen from the obtained device  $V_{\text{oc}}$ , the previously measured low recombination level has not been achieved at the cell level in these initial attempts.

As a way forward, previously reported measurements of the contact resistivity of  $MoO<sub>x</sub>$  on p-type silicon [3] suggest that smaller area contacts (for example 5% contact fraction) would not significantly increase the total cell series resistance. This would allow the use of a partial rear  $Mo_{x}$  contact on a p-type cell, with the remainder of the surface being passivated with a high quality passivation layer (for example  $Al_2O_3$ ).



Fig 2 – Representative light IV characteristics and curves for a.) 3 x 3 cm moly-poly and b.) 2 x 2 cm moly BSR cell architectures.

## **4. Conclusion**

The two proof-of-concept devices presented here demonstrate the use of  $SiO<sub>x</sub>$  / MoO<sub>x</sub> (on n-type silicon) and MoO<sub>x</sub> (on p-type silicon) contacts to c-Si solar cells. Efficiencies of 16.7% (3 x 3 cm) and 16.4% (2 x 2 cm) are achieved on n and p-type substrates respectively. Although modest in terms of performance, the results show that reasonable passivation and good transport can be simultaneously achieved with  $MoO_x$  and  $MoO_x/SiO_x$  structures. Indeed they demonstrate that  $MoO<sub>x</sub>$  could act as a suitable alternative to Al-alloyed and B-diffused  $p<sup>+</sup>$  regions.

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