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Low-temperature atomic layer deposition of MoO_x for silicon heterojunction solar cells

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The preparation of high-quality molybdenum oxide (MoO_x) is demonstrated by plasma-enhanced atomic layer deposition (ALD) at substrate temperatures down to 50 °C. The films are amorphous, slightly substoichiometric with respect to MoO_3, and free of other elements apart from hydrogen (<11 at%). The films have a high transparency in the visible region and their compatibility with a-Si:H passivation schemes is demonstrated. It is discussed that these aspects, in conjunction with the low processing temperature and the ability to deposit very thin conformal films, make this ALD process promising for the future application of MoO_x in hole-selective contacts for silicon heterojunction solar cells.

1 Introduction

In conventional silicon heterojunction (SHJ) solar cells, charge carrier selectivity towards either electrons or holes is achieved by applying n- and p-type doped a-Si:H layers, respectively, on top of very thin intrinsic a-Si:H passivation layers [1]. However, parasitic absorption of light in the a-Si:H layers severely limits the short circuit current density J_{sc} of such a cell [2]. A highly promising route to reduce this parasitic absorption is to replace doped a-Si:H by highly transparent metal oxides that provide charge carrier selectivity through band alignment and band offsets instead of doping [3–7].

Most notably, evaporated substoichiometric molybdenum trioxide (MoO_x) has recently attracted much attention. This material is highly transparent and selective towards holes due to its high workfunction [3–5]. Battaglia et al. have shown an increase in J_{sc} of 1.9 mA/cm^2 when replacing a-Si:H(p) by evaporated MoO_x which is due to reduced parasitic absorption. The MoO_x still has to be combined with a thin layer of intrinsic a-Si:H in order to obtain a high open circuit voltage V_{oc}, since MoO_x does not provide surface passivation [4, 5]. However, the deposition of conformal, non-porous ultrathin (<10 nm) films on textured surfaces by evaporation is very challenging.

The stringent requirements on thickness, conformality and density make atomic layer deposition (ALD) an ideal candidate for the deposition of such films as already suggested in the initial report on MoO_x by Battaglia et al. [3]. In addition, ALD has recently gained a strong foothold in the photovoltaics industry with the introduction of high volume manufacturing ALD tools for Al_2O_3 passivation layers [8, 9]. Even though ALD recipes for MoO_x have been reported in the last years, none of these recipes focus on low processing temperatures required for compatibility with the commonly used a-Si:H passivation layers [10–12].

In this work we report on a plasma-enhanced ALD (PE-ALD) process to deposit high-quality MoO_x at low temperatures down to 50 °C. Firstly, the deposition process is described and the film composition, morphology and optical properties are discussed. Next, the potential of the process for depositing ultrathin MoO_x in passivating contacts is explored by performing lifetime measurements on a stack consisting of an a-Si:H passivation layer, an ALD MoO_x layer as hole-selective layer and an ALD In_2O_3:H film as transparent conductive oxide. As will be shown, such stack combines a high level of surface passivation with an excellent optical light incoupling into the silicon absorber material thanks to the high transparency of both ALD-prepared metal oxides.

2 Experimental details Slightly substoichiometric molybdenum trioxide (MoO_x) was deposited by a plasma-assisted ALD process using $(NtBu)_2(NMe_2)_2Mo$ as Mo precursor and O_2 plasma as oxidant in a home-built ALD reactor [13]. The reactor has an inductively-coupled plasma source and is pumped to a base pressure of $<7.5 \times 10^{-3}$ mTorr by a turbomolecular and rotary pump. The precursor is delivered to the chamber by Ar bubbling from a precursor pot heated to 50 °C through gas delivery lines that are heated to 80 °C. The substrate temperature has been varied between 50 and 200 °C. The chamber walls are heated to 50 °C for depositions at a substrate temperature of 50 °C, or to 100 °C for higher deposition temperatures. The saturated precursor dosing time is 6 s at 7.5 mTorr (inset of Fig. 1), whereas saturation for the O_2 plasma step was reached within 4 s at 5.3 mTorr and 100 W plasma power. Purge times using Ar were 6 s and 3 s after the precursor dose and plasma exposure steps, respectively.

The film thickness, growth per cycle (GPC) and optical constants of the MoO_x films have been determined from spectroscopic ellipsometry using a Tauc–Lorentz oscillator to model the band-to-band absorption, and an additional Gaussian oscillator to account for weak subgap absorption, which is attributed to oxygen-vacancy-derived defects [3]. Lifetime measurements were performed using a Sinton WCT-120TS lifetime tester. Films were deposited on c-Si(p) wafers with native oxide. For the lifetime samples, floatzone c-Si(100) wafers (n-type, 285 µm, 3 Ω cm) were used as substrates, from which the oxide was removed by a one minute dip in 1%-dilute HF.

Intrinsic a-Si:H passivation layers were deposited by inductively-coupled plasma chemical vapor deposition (ICP-CVD) in an Oxford Instruments PlasmalabSystem100 ICP 180 at 50 °C from pure SiH_4. Amorphous In_2O_3:H (a-In_2O_3:H) was made by thermal ALD in an Oxford Instruments OPAL tool at 100 °C using InCp, H_2O and O_2 [14]. The a-In_2O_3:H films were subsequently crystallized (c-In_2O_3:H) by a 10 minute anneal at 200 °C in N_2, which yields a very high Hall mobility of 138 cm^2/V s at a device-relevant carrier density of 1.8×10^{20} cm^{-3}. Due to the extremely high electron mobility, c-In_2O_3:H combines a very low resistivity (0.27 mΩ cm) with negligible free carrier absorption, as reported recently [14].

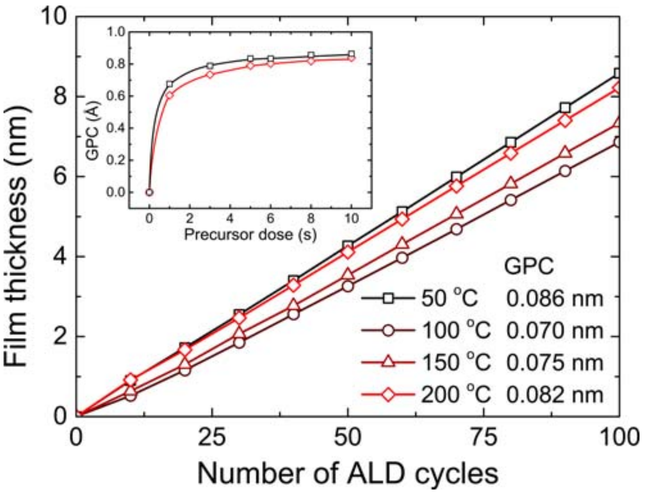

Figure 1 MoO_x film thickness as a function of the number of ALD cycles for deposition temperatures between 50 °C and 200 °C. The GPC for each temperature is indicated. Inset: Precursor dose saturation curves for 50 °C and 200 °C.

3 Results and discussion In Fig. 1, the MoO_x film thickness is shown as a function of the number of ALD cycles for temperatures between 50 °C and 200 °C. As can be seen, for all temperatures linear growth is achieved with relatively high growth per cycle (GPC) values of around 0.08 nm. The slight variation of the GPC with temperature is consistent with Rutherford backscattering (RBS) analysis of the amount of Mo atoms deposited per cycle (~1.4 Mo atoms nm^{-2} $cycle^{-1}$). Figure 1 also shows that there is no nucleation delay, which facilitates an accurate control over the MoO_x layer thickness even for very thin films.

For all deposition temperatures, the incorporation of N and C contaminants was found to be below the detection limit of RBS measurements (3 at% and 2 at% respectively), which demonstrates the high purity of the films. All films deposited in this temperature range are amorphous, as confirmed by X-ray diffraction and Raman spectroscopy measurements (not shown). Additionally, all films have an O/Mo ratio of ~2.9 as determined by RBS and are thus slightly substoichiometric with respect to MoO_3. The presence of oxygen vacancies in the substoichiometric matrix was confirmed by an observable shoulder in the Mo $3d_{5/2}$ peak in the XPS spectra (not shown) [3]. Note that an influence of ambient on the stoichiometry cannot be excluded as samples were not transferred *in vacuo*. Moreover, elastic recoil detection analysis has revealed a H content around 11 at% for the sample deposited at 50 °C, which decreased to 3 at% when going to 200 °C.

For the remainder of this article, we focus on MoO_x films prepared at the lowest temperature of 50 °C, as the low temperature is the main merit of this ALD process and as this temperature also yields the highest GPC. The properties of the films prepared at 50 °C are summarized in Table 1.

Table 1 Summary of the properties of a 20 nm MoO_x film deposited at 50 °C.

parameter	value
refractive index *n* at 2 eV	1.97
extinction coefficient *k* at 2 eV	1.94×10^{-4}
Tauc bandgap	2.9 eV
O/Mo ratio	2.95
H content	10.6 at%
mass density	3.95 g/cm^3
phase	amorphous

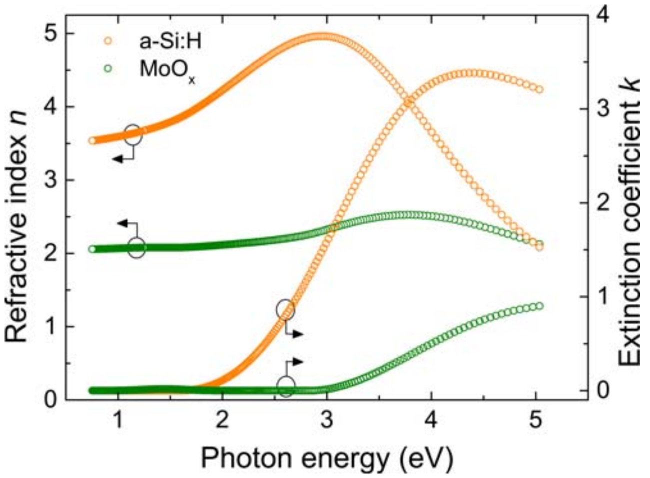

Figure 2 Refractive index n and extinction coefficient k of ALD MoO$_x$ as determined from *in-situ* spectroscopic ellipsometry. The optical constants of a-Si : H are shown for comparison.

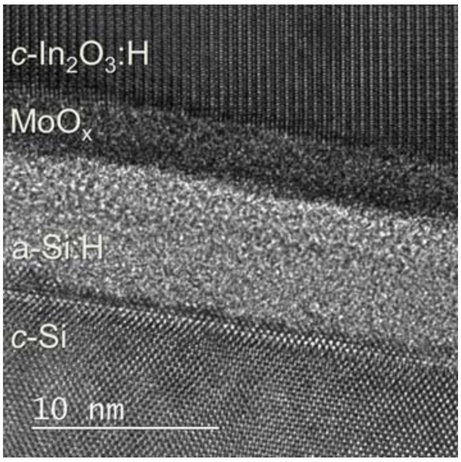

Figure 3 High resolution cross-sectional TEM image showing the passivating a-Si : H/MoO$_x$/c-In$_2$O$_3$: H stack on c-Si. As can be seen, the ALD process allows for the deposition of a very thin uniform MoO$_x$ layer.

Figure 2 shows a comparison of the optical constants of MoO$_x$ and a-Si : H, as obtained from spectroscopic ellipsometry. As can be seen, the refractive index n of MoO$_x$ is close to 2, which is ideal for efficient light incoupling into the high-index c-Si substrate. Additionally, the extinction coefficient k is much lower for MoO$_x$ than for a-Si : H and the bandgap is significantly higher. Therefore, strongly reduced optical losses due to both less light absorption and reflection are expected for MoO$_x$ in comparison to a-Si : H.

The potential for this process for the implementation of MoO$_x$ in passivated hole contacts for SHJ solar cells has been evaluated by determining the passivation performance and light incoupling for a stack similar to the stack of Battaglia et al. [4]. The stack consists of an a-Si : H passivation layer, an ALD MoO$_x$ film to serve as hole selective layer and an ALD c-In$_2$O$_3$: H film as transparent conductive oxide. The as-deposited, amorphous In$_2$O$_3$: H film, which was 75 nm thick, has been crystallized by annealing at 200 °C for ten minutes in order to obtain excellent optoelectronic properties [14]. A high resolution cross-sectional TEM image of the stack after the full process is shown in Fig. 3.

As can be seen, the a-Si : H layer forms a sharp interface with c-Si, which is prerequisite for good surface passivation after post-annealing [15]. The MoO$_x$ layer is uniformly deposited on top of the a-Si : H layer and has remained amorphous during the post-annealing step for the whole stack. At the a-Si : H/MoO$_x$ interface an increased contrast can be observed, which could suggest that some layer intermixing has taken place, either during deposition of the MoO$_x$, during post-annealing or during focused ion beam preparation of the TEM sample. The crystallized In$_2$O$_3$: H film shows a very defect-free crystal structure, in line with our previous results [14].

In order to evaluate the passivation quality of the stack in Fig. 3, the injection-dependent minority carrier lifetime has been tracked after each processing step, as shown in Fig. 4. As evidenced by a high implied V_{oc} of 722 mV, the a-Si : H layer offers an excellent level of surface passivation. After the deposition of MoO$_x$ a significant decrease in passivation is observed. This is attributed to plasma-induced damage during the O$_2$ plasma step in the PE-ALD process [16, 17]. Note that for this lifetime sample, milder plasma conditions (7.5 mTorr pressure, 48 W power, 2 s exposure) were used to mitigate plasma-induced damage to the a-Si : H layer, which did not result in an observable effect on the GPC or film properties studied.

Although the damage by the plasma process is a disadvantage with respect to thermal ALD (without plasma), the plasma-induced damage to the a-Si : H passivation layer can fortunately largely be recovered after the deposition of In$_2$O$_3$: H by the subsequent thermal crystallization step

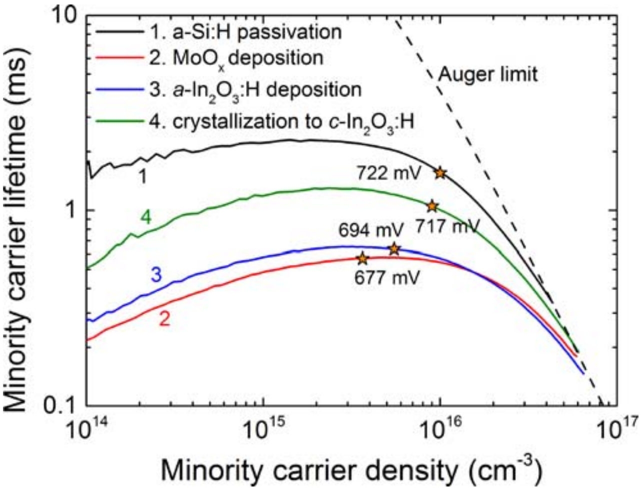

Figure 4 Injection-dependent minority carrier lifetime after subsequent processing steps during the preparation of the a-Si : H/ MoO$_x$/c-In$_2$O$_3$: H stack. The star symbols indicate the implied V_{oc} under 1 sun illumination.

[17–19]. After the final step, a promising high implied V_{oc} of 717 mV is achieved, which demonstrates the high level of surface passivation that can be achieved for such a stack.

The expected improvement in J_{sc} when replacing a-Si:H(p) by ALD MoO_x has been assessed by optical simulations on the light incoupling into a solar cell using the PVLighthouse OPAL 2 calculator [20]. For the simulations, a surface consisting of random upright pyramids was chosen, along with a normally incident AM1.5g spectrum. For the stack in this work, a promising active-area J_{sc} of 41.7 mA/cm^2 is predicted, very close to the maximum absorbable photon current of 44.0 mA/cm^2 present in the AM1.5g spectrum. In addition, this is significantly higher than the 41.2 mA/cm^2 and 40.7 mA/cm^2 calculated for a very thin 5 nm or more commonly-used 10 nm a-Si:H(p) layer, respectively.

4 Conclusions A new PE-ALD process for the deposition of MoO_x at low temperatures has been presented. The deposited films are free of C and N contaminants and slightly sub-stoichiometric with respect to MoO_3. Films deposited at 50 °C contain 11 at% of H. A promising high implied V_{oc} of 717 mV was achieved with a stack of a-Si:H/MoO_x/c-In_2O_3:H, in which the MoO_x was deposited using the newly developed ALD process. Optical simulations have predicted an exceptional active-area J_{sc} of 41.7 mA/cm^2 due to the good optical properties of both MoO_x and c-In_2O_3:H. This shows the high potential of this new ALD process for the implementation of MoO_x in solar cells with passivated hole contacts. Future work will focus on the verification of hole-selectivity of the ALD MoO_x films and on the implementation of stacks with ALD MoO_x in SHJ solar cells.

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