MoO_x thin films deposition by reactive RF-magnetron sputtering

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Abstract: Sub-stoichiometric molybdenum oxide (MoO_x, $x < 3$) thin films are deposited and analyzed to find optimum parameters for its use in heterojunction solar-cells. Deposition is done on n-type crystalline silicon wafer and glass substrates by reactive RF-magnetron sputtering. Oxygen partial pressure and deposition pressure are the two parameters used to vary stoichiometry influencing other characteristics. Stoichiometric composition, thickness, electrical properties and optical response have been studied to characterize the deposited thin films. MoO_x, as other transition metal oxides, on the n-type silicon wafer act as a hole-selective layer. It is a good way of providing a p^+-n junction without using dopant.

I. INTRODUCTION

Crystalline silicon (c-Si) has been the main material in solar cell technology. Its band-gap of 1.1 eV allows the absorption of a big part of the solar spectrum light. The traditional silicon solar cell technology consists in the diffusion of a dopant into the silicon wafer to create a p^+-n junction[1]. Diffusion process needs high temperature, so thermal expansion and consequent wafer curvature or break could compromise the evolving tendency of thinning c-Si wafers. Use of silicon heterojunctions (SHJ) solar cells has been a solution, specifically Panasonic's HIT model (registered trade mark of the Panasonic group) that demonstrated efficiencies of up to 25% [2]. A hydrogenated amorphous silicon p-type layer (p a-Si:H) is deposited on the top of n-type c-Si and a n^+-type in the bottom (n^+ a-Si:H). The p-doped layer acts as a hole transport layer (HTL) and n-doped layer as an electron transport layer (ETL). Recently, transition metal oxide's (TMO) deposition has been proposed as an easy alternative to the use of toxic gases as B_2H_6 or PH_3 in HIT. In this technology p layer is substituted by a TMO layer that act as HTL, by blocking electrons and transferring holes. Different TMOs used as HTL are molybdenum, vanadium or tungsten oxides[3]. Also the n^+ layer can be substituted by other ETL like titanium oxide or lithium fluoride.

In this work we study MoO_x ($2<x<3$) on n-type crystalline Silicon (c-Si) solar cells. Oxygen vacancies push MoO_x, with a wide gap (i.e. 3eV)[3], to act as an n-type semiconductor with a Fermi level near the conduction band. Abrupt work function disruption in the interlayer due of the large difference between MoO_x work function (6.5eV) and n-Si work function ($\sim$4.2eV) produce an electrical potential induced (band bending) that drains silicon's surface of electrons and

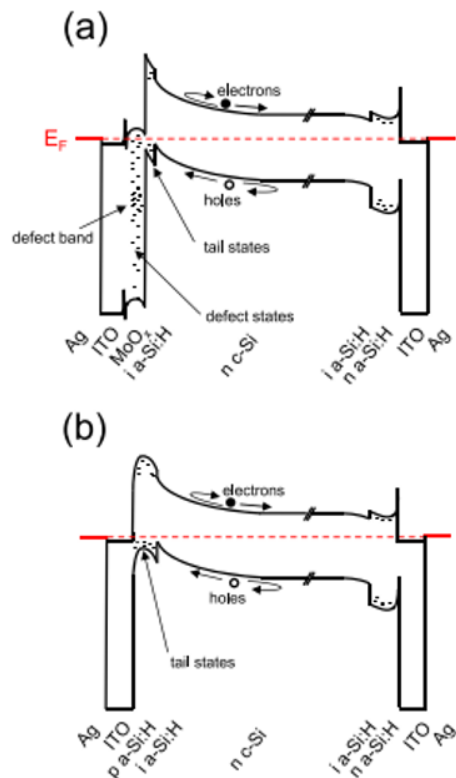

FIG. 1: Energy band diagrams for c-Si with hole selective (a) MoO_x contact and (b) standard p-type a-Si:H emitter.[5]

creates a p^+ layer[3][4]. When a photon is absorbed in the silicon, an electron transits from the valence band to the conduction band, the high work-function of the TMO disables the electron to pass to the HTL, MoO_x in this case. Otherwise, the holes conduction is improved thanks to oxygen vacancies[4]. This phenomenon that takes place in the solar cell is represented with a diagram of energies in FIG.1a contrasted with an standard SHJ in FIG.1b.

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A thin intermediate intrinsic layer of hydrogenated amorphous silicon (a-Si:H) between the oxide contact and the silicon absorber is inserted (MoOx/a-Si:H/c-Si). This layer protects the silicon surface, diminishes the interface traps and increases the efficiency from 14.3% to 18.8% according to Battaglia's work[5]. This layer inserted by plasma enhanced chemical vapor deposition (PECVD) is, in our case, also a physical protection to the bombardment of high-energy ions produced in the sputtering deposition[6].

Some earlier studies explain that changes in oxygen partial pressure change electrical, optical and stoichiometric characteristics of TMOs[3]. A sample MoO_2 (Mo^{4+}) is almost nontransparent with metal electrical conductivity but a sample MoO_3 (Mo^{6+}) is transparent and insulator. The aim of our work is to study the characteristics of these changes[3].

There are different options to deposit the MoO_x on the wafer. The most common is evaporation but magnetron sputter deposition (MSD) is an easier alternative for industrial application and allows a good composition control[7]. An earlier study used MSD with a ceramic target (MoO_3)[8]. The temperature was used to change O/Mo relation but a high temperature was required to create oxygen vacancies. That's why a reactive MSD method has been chosen for this work. A molybdenum metallic target has been used and oxygen partial pressure as well as deposition pressure have been varied to control the composition of the films. It can be a good solution for industrial applications.

II. EXPERIMENTAL

Different series of samples with different characteristics varying oxygen/argon gas flow ratio were deposited. The interval of oxygen was delimited by a previous study to ensure in which values MoO_x is a semiconductor. As it can be seen, it easily becomes quasi metallic. The substrates used were doped n-type silicon (FZ, 100mm diameter, 1-2Ω-cm resistivity, 280μm thickness). Corning glasses (1737 F) were also introduced to allow the study of optical and some electrical properties.

The main instrument used in the deposition was a radio frequency magnetron sputtering, specifically an ATC ORION 8 HV confocal sputtering with 3 guns. Only a metallic molybdenum target was used (Mo, size: 7.62cm diameter x 6mm thickness, typical purity: 99.95%) and a pressure around 0.2 Pa in deposition. Before deposition, c-Si substrates were cleaned following RCA (Radio Corporation of America) method with a final 1% hydrofluoric acid solution cleaning of 60-s just before deposition. Plasma is turned on by a radio frequency signal of 13.56MHz that arrives at the gun and excites the electrons that will collide with argon gas and create Ar^+ ions. In this kind of sputtering an array of magnets is situated behind the target, producing a magnetic field that conserves the plasma near the target[9]. In this case, we choose 90-100W power for a surface of 45.6cm^2, that is limited power density of 2.2W/cm^2, to not damage the substrate. It is located at 18 cm away from the target, with a rotation of 13rpm on its own axis. This popular technique allowed us to deposit highly uniform samples, to have more control over thickness and to deposit different materials with no need of target re-position[10]. The machine is located in the Laboratory of Micro and Nanotechnology of the Universitat of Barcelona, with characteristics of 200m^2 ISO 7 (10000-Class).

To start the analysis thickness was measured using a mechanical surface profiler equipped with a stylus (Alpha-Step D-120 Stylus Profiler). Ellipsometry using the changes in phase of a coherent light beam after being reflected was also used when necessary.

Then, X-ray photo-electron spectroscopy (XPS) gave the deposited films final stoichiometry. X-rays that excite electrons are sent to the sample area. Measuring the electrons' kinetic energy of those that escaped, the atomic composition and the chemical state of the atoms in the material can be deduced. To generate atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity by a relative sensitivity factor (RSF), and normalized over all of the elements detected[11]. The specific machine used was a PHI 5500 Multitechnique System (Physical Electronics®) with a monochromatic X-ray source (Aluminium K-α line of 1486.6eV energy and 350W), placed perpendicular to the analyzer axis and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 0.8eV.

The balance between high optical transparency and good conductivity has always been the main problem of the photo-voltaic technology. On one hand, to study the optical response of the sample, an spectrophotometer(LAMBDA 950) that gives the spectrum of frequencies absorbed was used. The absorption coefficient was found measuring reflectivity (R) and transmittance (T) in the wavelength range of 200-1500nm and using the equation (1) where t is the thickness. This relation is an approximation used when the product αt is large[12]. A seen in FIG4b, plotting $(\alpha E)^2$ vs E, where E is energy, and following the Tauc's equation (2), the energy gap E_g can be found. A is a constant and n=2, as a parameter that indicates an indirect gap.

$$\alpha = \frac{1}{t} ln \frac{(1-R)^2}{T} \tag{1}$$

$$\alpha E = A(E - E_g)^n \tag{2}$$

On the other hand, transfer length measurements (TLM) were used to obtain an accurate conductivity's value. Several parallel metallic contacts with different spacing distances (*d)* are evaporated on the film to be analyzed, and current is measured at different voltages applied between every pair of contacts. FIG5a shows the procedures. TLM can be measured on samples deposited on glass or on silicon. In the first case, current flows throw the MoO_x. If deposition's thickness is known, the conductivity of the MoO_x is found from glass. Then, by measuring the films deposited on silicon, electrical properties of the inversion layer can be deduced. If inversion layer is much more conductive than MoO_x, current between the contacts flows through the inversion layer. Supposing this approximation, the same equation as in glass was used (3). Otherwise, the current would flow in parallel through both regions, and can be described as two resistances in parallel. W is contact width known and d the distance between the contacts. In the limit of a zero-length resistor, the residual resistance would be just twice the contact resistance.

$$R_T = R_{sc} + 2R_c = \frac{R_S d}{W} + 2R_c \qquad (3)$$

Lastly, passivation of the Si surface by MoO_x layer was estimated by measuring the lifetime of Si wafers passivated with an a-Si:H layer on one side and the MoO_x layer on the other. Symmetrical samples with a-Si:H layers on both sides exhibit lifetimes in the order of 1ms. A WCT-120 Photoconductance Lifetime Tester from Sinton Consulting.Inc was used to measure. After a flash light, recombination of the pairs electron-hole does not occur immediately and varies with each material. Quasi-Steady State is the approximation used. Effective lifetime vs. carrier density was plotted knowing that generation rate multiplied by effective lifetime is proportional to photoconductance[13].

III. RESULTS AND DISCUSSION

A constant velocity was assumed along the film growing process. Deposition rates are between 3-5 nm/min when deposition pressure is 0.27Pa and oxygen partial pressure in the 4-7% range, as well at 3.5% of oxygen partial pressure and a deposition pressure in a range of 0.2-1.3Pa.

XPS gave us a survey spectrum that showed all the element in the sample surface. Carbon, oxygen and molybdenum peaks were specifically analyzed. In FIG.2a stoichiometric composition evolution of molybdenum is plotted in the line $3d^{5/2}$ and $3d^{3/2}$. Intensity area derived from XPS results was calculated by CASAxps.exe[14] program referencing the C 1s peak to 284.8eV. Deconvolution Gaussian peaks were used

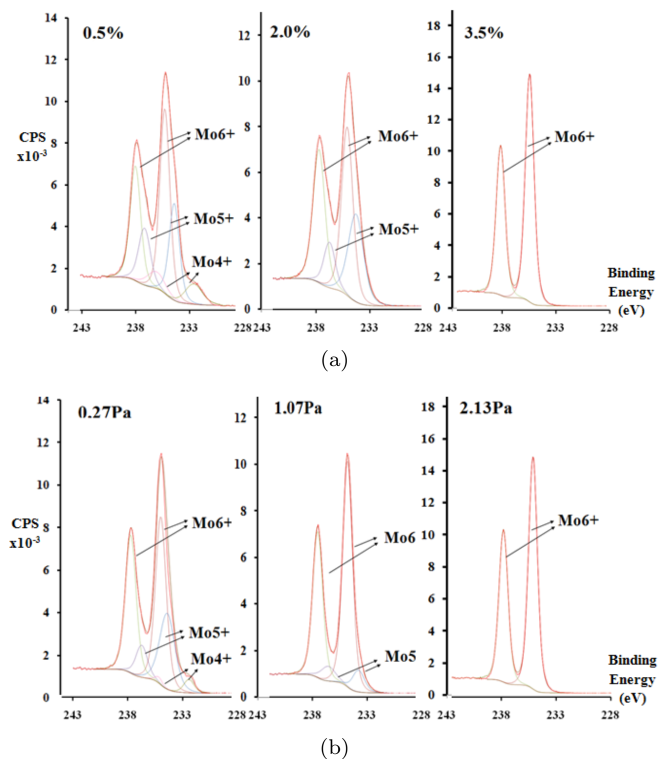

FIG. 2: XPS analysis: (a)Evolution of Mo at 2,13Pa and power of 90W. In order, 0.5% 2.0% and 3.5% oxygen partial pressure. (b)Evolution of Mo at 3.5% of oxygen partial pressure and power of 90W. In order: 0.27Pa, 1.07Pa and 2.13Pa pressure deposition.

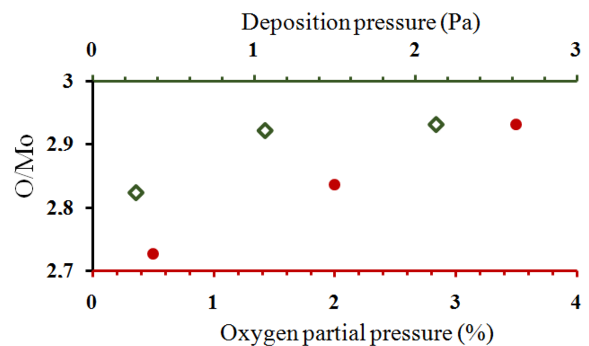

FIG. 3: Oxygen relation with molybdenum at power of 90W, as a function of oxygen partial pressure at 2.13Pa (•) and deposition pressure at 3.5% oxygen partial pressure(⋄).

to model the results. Part of the oxygen is bonded with carbon, so we subtracted the carbon's peak that is bonded with oxygen ((C=O) min: 288.0eV, max: 289.2eV)[11] from the oxygen area. The results of O_x/Mo evolution are shown in FIG.3. The more oxygen partial pressure there is in the sputtering's chamber, the closer the sample is to MoO_3. The same happens with the increase of pressure deposition. When there is more pressure in the chamber, oxygen ions collide

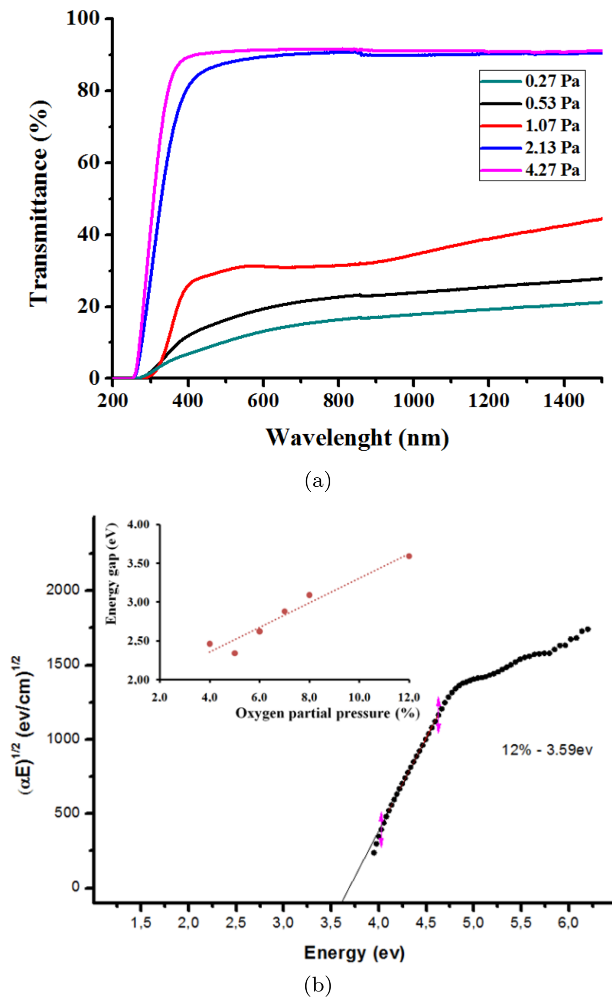

FIG. 4: (a) Transmittance for differents pressures at 3.5% oxygen partial pressure and power of 90W.(b) Procedures to find energy gap for the series at 0.27Pa and power of 100W.

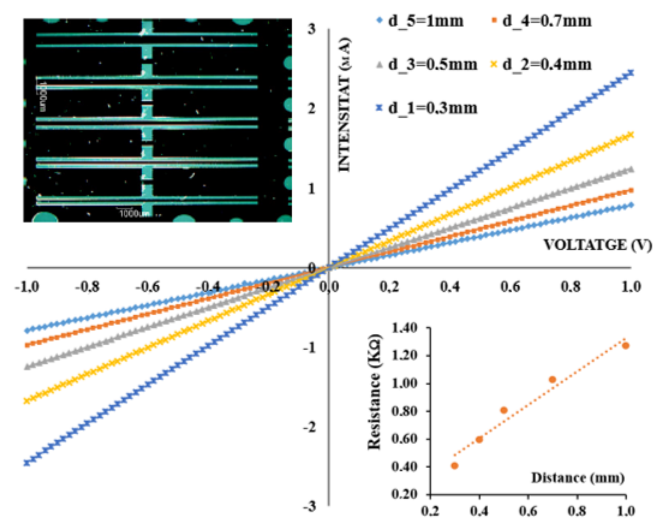

FIG. 5: Photo of TLM contacts on Silicon wafer. I(V) and R(d) of sample deposited at 4.27Pa and 3.5% oxygen partial pressure at 90W on glass.

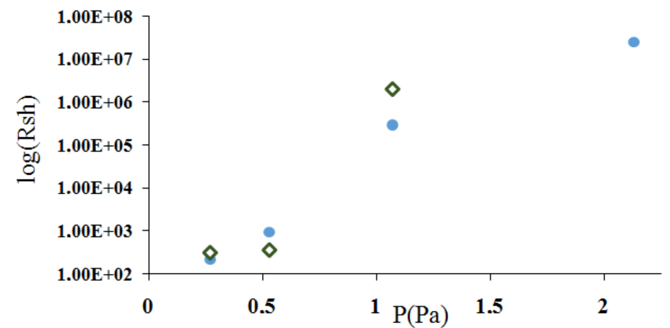

FIG. 6: Resistance sheet of the inverse layer according of pressure deposition at 3.5% oxygen partial pressure at 90W. Calculated on Silicon(•) and on glass (∗)

more frequently with Mo ions, being easier to create MoO_3. Note the presence of Mo^{5+} as first symptom of oxygen's vacancies. With less oxygen partial pressure, we can observe also the Mo^{4+} peak, meaning presence of MoO_2. If the evolution against pressure is observed, there is clearly a similar change in stoichiometry. When deposition pressure increases, the material becomes more stoichiometric. Our interest was to avoid having pure MoO_3 in order to have vacancies. That turns molybdenum oxide into a hole-selective contact. The oxygen vacancies act as donor impurities and the junction MoO_x-silicon becomes a barrier for the electrons[15].

Optic response changes with the oxygen partial pressure and deposition pressure. These variations are caused by stoichiometry changes. MoO_x film become more transparent with the increase of oxygen, as well as with deposition pressure. Some results of these measurements are presented in FIG.4a. A higher transmittance, specially in the U.V. part of the spectrum, means lower optical losses and favors photo-generation in the active layer. Energy gap was calculated from Tauc's equation, as explained in the instrumental section. The inset in FIG.4b shows an example of optical gap evolution. The gap increases with oxygen partial pressure and deposition pressure, as does the trend of transmittance. As expected, the gap is around 3eV, This is a clear advantage of MoO_x in comparison to doped a-Si in HIT cells, since optical losses in the UV region are clearly decreased[3]. An oxygen partial pressure series in FIG4b is shown as example.

TLM measurements show also the control obtained during the sputtering process. Resistance increases with increasing oxygen percentage and deposition pressure. Varying these two parameters, resistance of the inversion layer can be controlled. The logarithmic scale graph in FIG6 shows the sheet resistance measured in silicon and in glass. For low pressure, MoO_x (lower

x values) exhibits a metallic behavior, so there is almost no resistance and there is no inversion layer. For high pressures, as 2.13Pa, MoO_x (with x closer to 3) is very insulator, so there is a huge resistance and it's impossible the current. But observing the intermediate range, as 1.07Pa point, the presence of inversion layer in silicon is deduced. Resistance in glass is considerably higher than in silicon. The resistance of inversion layer is calculated assuming MoO_x and inverse layer acts in parallel, as explained in the experimental section obtaining a value of 3.34×10^5 Ω/sh at 1.07Pa.

Oxygen partial pressure (%)	4.0	5.0	6.0	7.0	8.0	12.0
Lifetime (10μs)	15	15	16	18	8.4	19

TABLE I: Life time data of oxygen partial pressure variation at 0.27Pa and 90W of power.

Optical and electrical response is successfully controlled by the two parameters proposed. Lifetime measurements have been also studied as an approach to a final solar cell. As seen in table I, MoO_x lifetime results are in the order of μs and there is no clear trend. Knowing minimum lifetime condition in c-Si is ∼1ms[4], results are disappointing. This fact can be due to the creation of new defects on the silicon surface by ion bombardment during MoO_x deposition. However, this problem has been recently solved including a very thin a-Si:H deposited by PECVD on the wafer before sputtering. The addition of this simple step on the process improves significantly lifetime results. An effective lifetime of 1.5ms has been successfully obtained including an annealing step at 150°C during an hour. As explained in the introduction, a-Si:H layer protects and it can serve as a source of hydrogen atoms for surface chemical passivation. The use of mild conditions (lower power and higher pressure) in the initial stages of the sputtering deposition and progressively increasing power and reducing pressure can be an alternative to obtain an integral sputtering process. This strategy has been successfully applied for Al_2O_3 passivation in García-Valenzuela's work[6].

IV. CONCLUSIONS

Magnetron sputtering is a good alternative to evaporation. MoO_x electrical and optical properties have been well controlled by the parameters during deposition. When oxygen partial pressure, as well as deposition pressure, is increased; the molybdenum oxide (MoO_x) is more stoichiometric (MoO_3). Sub-stoichiometric molybdenum oxide (MoO_x) on n-type c-Si can be used as a good p^+-n junction as a hole-selective contact and, with the TLM results, we conclude the presence of an inversion layer in the MoO_x-Si interface. The introduction of an hydrogenated amorphous silicon film is an effective alternative to obtain good lifetime.

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