High Pressure Sputtering of materials for selective contacts in emerging photovoltaic cells

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***Abstract*— In this work we have explored the growth by high pressure sputtering (HPS) of materials intended for novel selective contacts for photovoltaic cells. This technique shows promise for the low-damage low-temperature deposition of PV materials. We studied the deposition of ITO, MoO_x and TiO_x using pure Ar and mixed Ar/O_2 atmospheres as well as ceramic or metallic targets. We show that HPS deposition of these materials is feasible. The growth rate is greatly reduced when oxygen is added to the argon sputtering atmosphere. The best sputtering RF power was 20-45 W for the pressure range studied. Finally, as-deposited films present high surface recombination, but a mild hot plate anneal at 200ºC recovers long effective lifetimes.**

Keywords—sputtering, photovoltaic cells, selective contacts.

I. INTRODUCTION

The understanding of the physical behavior of photovoltaic cells is a topic that has evolved rapidly during the last decade. In particular, the photovoltaic community has reached the consensus that the pn junction electric field is not necessary for the photovoltaic effect. Now we know that an efficient solar cell only needs a good absorber sandwiched by two membrane-like structures, each one permeable to only one type of carrier (electrons or holes). These membranes are the so-called selective contacts (SC) [1].

At present, there is research on many materials that show this selective character when they are grown on c-Si. The most promising ones are MoO_x for hole transport layer (HTL), and TiO_x for electron transport layer (ETL) [2]. However, these oxides typically degrade when exposed to air, so in situ capping is also very interesting. This capping can be metallic and/or transparent.

In this article we show our results on the deposition of TiO_x, MoO_x and ITO by a non-conventional technique such as HPS [3],[4]. By the increased pressure the energetic species present in the plasma thermalize before reaching the substrate. This way surface damage can be minimized. This technique is specially fitting for the SC deposition because it can also be used for the growth of high quality ITO and/or metallic films. Therefore, either transparent conductive or metallic capping layers can be deposited sequentially [5] in the same system, thus minimizing interfacial degradation, which is critical for an efficient photovoltaic cell.

II. EXPERIMENTS

We have sputtered these materials on transparent glass for plasma and growth characterization, on c-Si wafers for ellipsometric measurements, and on a-Si:H passivated n-Si wafers for lifetime measurements. We did not intentionally heat the substrates during growth. The substrate temperature increased due to plasma heating, but for all samples it was always lower than 80 ºC. The available targets (provided by Kurt J. Lesker) were 2” diameter disks of ITO, metallic Ti and metallic Mo. The compact design of HPS enables the installation of all three targets in a single deposition chamber. Sequential deposition is feasible with the aid of a programmable motor. The high pressures minimized cross-contamination of the targets. The sputtering atmosphere was

pure Ar or mixed Ar/O_2. We studied the effect of pressure variations (in the 0.1 mbar to 2.3 mbar range) and RF power (from 5 W to 50 W). The plasma was characterized by glow discharge optical spectroscopy (GDOS). The films were characterized by profilometry, ellipsometry and sheet resistance measurements. Finally, the minority carrier lifetimes of selected samples were measured by the quasi-steady-state photoconductance method. The structures were measured before and after a 200ºC hot-plate anneal 30 min long, without atmospheric control.

III. Results

Fig. 1 shows the GDOS spectrum in the 200 nm – 600 nm wavelength range when the sputtering is done in pure Ar atmosphere at a pressure of 0.5 mbar. We observe that when ionized Ar is present all the relevant species (In, Sn, Mo and Ti) are extracted [6]. We have measured these spectra at pressures in the 0.1 mbar – 2.3 mbar range and concerning species extraction there are not relevant differences.

As expected, the Mo and Ti films were metallic with low transmittance in the visible. Focusing on the ITO spectrum no clear O signal could be detected, because O emissions in the studied wavelength range are close to Ar+ emissions. An oxygen deficient ITO would present low resistivity and poor transparency. In our case, the films were transparent for all pressures and with reasonable resistivity for pressures over 1.0 mbar, under 10^{-3} ohm.cm. This fact indicates that there was enough oxygen for the oxidation of the ITO film. The understanding of the resistivity dependence on Ar pressure is a topic that we will study in the future.

To determine the optimal RF power we focused on the integrated area of relevant peaks for each material. For instance, fig. 2 shows how the Ti target needs at least 20 W to commence deposition. Also, it is not efficient to work at RF power higher than 40-45 W, as the integrated intensity of the Ti-related peaks located in the 397.5-401.8 nm range shows. The intensities for different pressures should not be quantitatively compared since the plasma shape depends on pressure, and this shape change affects the amount of light that reaches the optical fiber. Thus, we found that the growth rate depends on pressure, and as the pressure increases the growth rate decreases. The growth rates found were in the 10^{-1} – 1 nm/min range, adequate for thin film deposition, since most SC materials are ~ 3-10 nm thick [7], [8]. Metallic Mo showed an analogous trend.

Once that we have found that HPS is able to deposit metallic Ti and Mo films, we will focus on the fabrication of their oxides. To achieve this there are at least two options available: in a conventional approach the oxides can be directly grown with a mixed Ar/O_2 atmosphere, or either the metallic films can be oxidized in situ by an oxygen plasma [9]. Fig. 3 shows that introducing O_2 to the gas mixtures produces the disappearance of the Ti and Mo peaks. This in is an indication of a much-reduced Ti and Mo extraction, and consequently a reduced growth rate. Figs. 1 and 3 should not be quantitatively compared since the spectra are normalized to the maximum intensity. The spectra in figure 3 are much less emissive. As a reference, the OH peak in fig. 1 is hardly appreciable, but it is dominant in fig. 3.

For these conditions ellipsometry (not shown) demonstrates that transparent films are growing with the mixed Ar/O_2 atmosphere (TiO_x or MoO_x) but with a reduced growth rate. On the other hand, after testing many plasma oxidation conditions at room temperature on metallic Mo films, the sheet resistance measurements showed that metallic Mo did not show any measurable oxidation. Thus, to obtain MoO_x by HPS we have to rely on the conventional Ar/O_2 approach. On the other hand, thin metallic Ti films increase their sheet resistance with relatively short plasma oxidations, indicating that for TiO_x deposition plasma oxidation is also a possibility.

Concerning film uniformity, we are limited by the target diameter: as is typical with sputtering, since we are using 2" targets the region with uniform deposition will be much smaller [10]. We have found that increasing pressure improves film uniformity for the metallic targets. For the MoO_x films, the in-wafer thicknesses differences in a central portion of the wafer with a diameter of 3.5 cm the thickness differences are less than 10% for pressures above 0.5 mbar. Fig. 4 shows an example of a thickness measurement by ellipsometry in these conditions.

However, for the ceramic target the pressure variations do not impact much on the film uniformity. Fig. 4 shows that at the same pressure as the metallic Mo target, when the ceramic ITO target is used the film uniformity is worse. Also, for this target the thickness profile does not change significantly when the pressure is varied (not shown). We can explain this behavior by the differences in conductivity of the targets: the metallic target has a very low resistivity, thus the RF power spreads evenly across its surface and thus the deposit is quite uniform. On the other hand, for the ceramic target, due to the lower conductivity of the material the RF power tends to concentrate in the surface closer to the backside plane. Due to the ground shield design of the system this plane does not cover the whole back surface of the target. To prevent this effect, a re-design of the target holder to include a whole-surface back-plane contact would be needed. In any case, there is a central region with an approximatively 2 cm diameter and thickness differences under 10%, which is adequate for the fabrication of small area research PV cells.

Finally, a key point to achieve an efficient PV cell is surface passivation, since in order to achieve carrier selectivity the surface recombination velocity must be low. Thus, as a first step we have evaluated whether HPS deposited ITO affects the passivation quality achieved by thin (~5 nm) intrinsic a-Si:H deposited by PECVD onto both sides of a c-Si wafer. The degradation is often observed with many sputtering processes. This sample presented a long lifetime of 1.8 ms before ITO deposition. As Fig. 5 shows, the lifetime degraded severely after ITO deposition. This degradation can be due to sputtering damage or UV radiation. The first type of damage is not easily recoverable, while the former can be repaired by a mild hot-plate anneal [11]. We found that for this sample the plasma damage must be low, since the passivated wafer reaches a minority carrier lifetime of ~1 ms after a 30 min 200ºC hot plate anneal.

IV. Conclusions

The results presented in this article indicate that HPS is a promising technique for the deposition of materials for emerging solar cells with non-doped selective contacts. In the future we will focus on material characterization, aiming at the fabrication of a dopant-free solar cell.

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