Physical and Electrical Characterization of Sputtered ITO Films for Use as Solar Cell Electrodes as Well as Interlayers in Low-Resistance MIS Contacts in Ge/Si Transistors

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ENGR 241 Project, Fall 2017
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1. Executive Summary

The goal of this project is to obtain RF-sputtered ITO recipes on the Lesker sputtering tool, a fairly new addition to the Exfab facility, that result in maximum conductivity and optical transmission over the solar spectrum (AM 1.5 spectrum). The applications requiring such characteristics are solar cells and low-resistance Metal-Interlayer-Semiconductor (MIS) contacts. Solar cells require ITO films with maximum conductivity and transmission over the solar spectrum to be used as the transparent electrode of the solar cell. In low-resistance MIS contacts ITO is used as the interlayer film. To achieve very low contact resistance, the conductivity of the ITO film should be maximized.

The optimal resistivity and transmission recipes found in this project are listed in table A. Please note that due to the semi-random distribution of transmission data - as explained thoroughly in the report - the optimal transmission recipe, in contrast to the optimal resistivity recipe, is not completely repeatable and thus reliable. You can find more details on this in the *Design of Experiments (DOE)* and *Repeatability Test* sections. Given its absorption coefficient value, the optimal transmission recipe results in 80% transparency over the solar spectrum for a 50 nm ITO film, which is pretty high compared to the ITO films used in the industry and academic research.

Table A. The optimal resistivity and transmission recipes of sputtered ITO fabricated by Lesker Sputter

Optimal Resistivity Recipe	
O_2/Ar Ratio	0
Pressure	3 mTorr
Power	100 W
Subs. Bias	50 V
Temperature	~ 70 ^{o}C (no heating)
Resistivity	4.8e-4 ohm.cm

Optimal Transmission Recipe	
O_2/Ar Ratio	0
Pressure	3 mTorr
Power	100 W
Subs. Bias	50 V
Temperature	270 ^{o}C
Abs. Coeff.	44400 cm^{-1}

Figure A and B respectively show how the resistivity and absorption coefficient of ITO films as well as their atomic composition change around the optimal resistivity recipe listed in table A. In each plot, one of the 5 factors of the optimal recipe (O_2/Ar ratio, pressure, power, substrate bias, and temperature) is varied around its optimal value. It can be seen in figure A that O_2/Ar ratio and pressure have the most significant effects on resistivity. Also, figure B shows that all factors have nearly the same effect on the absorption coefficient and thus the transmission.

The trends observed in figure A and B demonstrate that in general the more the tin content and the less the oxygen content of an ITO film, the more conductive it is. Also, more oxygen also generally results in higher optical transmission over the solar spectrum. Heating anneals the ITO films, further improving their optical transmission.

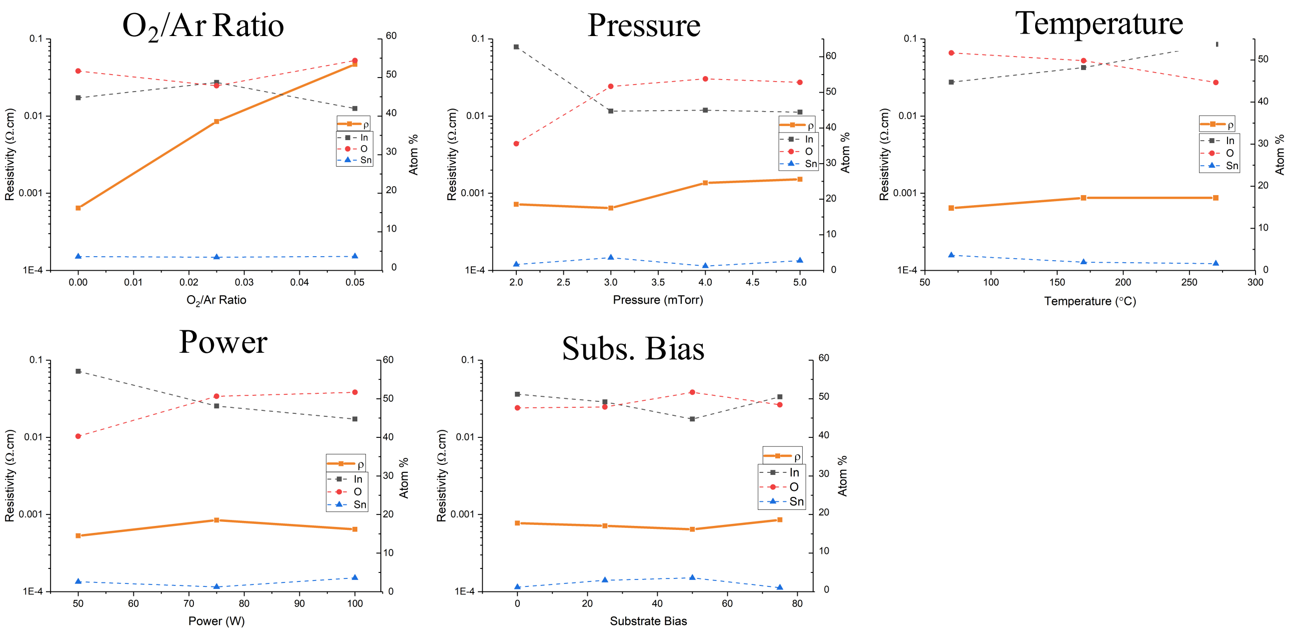

Figure A. Resistivity and atomic composition of sputtered ITO films around the optimal resistivity recipe

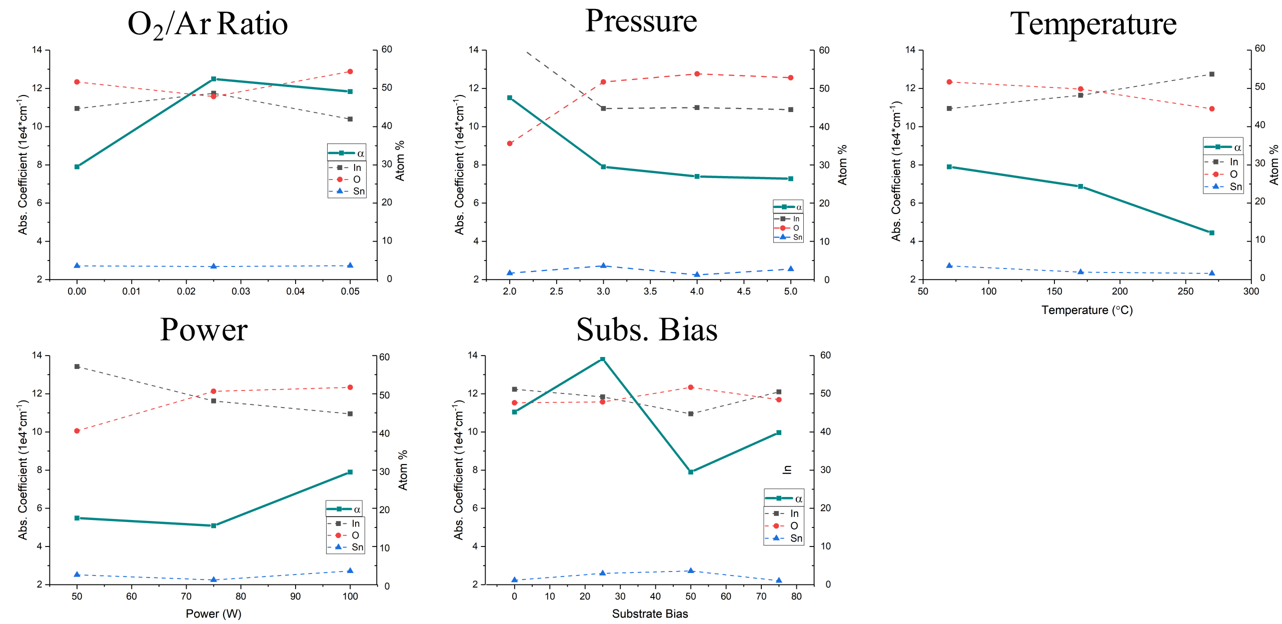

Figure B. Abs. Coeff. and atomic composition of sputtered ITO films around the optimal resistivity recipe

2. Introduction

The aim of this project is to obtain RF-sputtered ITO recipes on the Lesker sputtering tool, a fairly new addition to the Exfab facility, that result in maximum conductivity and optical transmission over the solar spectrum (AM 1.5 spectrum). The applications requiring such characteristics are solar cells and low-resistance Metal-Interlayer-Semiconductor (MIS) contacts. Solar cells require ITO films with maximum conductivity and transmission over the solar spectrum to be used as the transparent electrode of the solar cell. In low-resistance MIS contacts ITO is used as the interlayer film. To achieve very low contact resistance, the conductivity of the ITO film should be maximized.

In the upcoming chapters, we first discuss the motivation behind this project which was briefly mentioned above. Then we will give an overview of the process, followed by the Design of Experiments (DOE) methods used. After, discussing the repeatability of the experiments and measurements, we will present the final results and then a summary of the major findings of the project.

If you have any questions about the project or need help with sputtering highly conductive, highly transparent ITO films, please do not hesitate to contact us. We would be more than happy to help.

Best Regards,
December 2017
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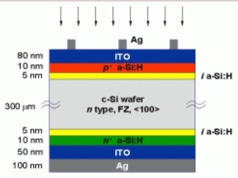
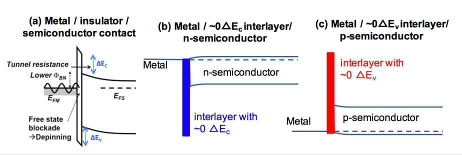
3. Motivation

ITO is widely used as a transparent electrode in solar cells both in the industry and academia. Stanford solar community is not an exception. Almost all solar research groups at Stanford use ITO in their solar cell structures. A high-quality ITO solar cell electrode is the one with maximum conductivity and optical transmission over the solar spectrum (AM 1.5 spectrum). To the best of authors' knowledge, since the solar researchers at Stanford do not have the knowledge/skill to fabricate high-quality ITO films using the equipment on campus, they either have their ITO deposition done by solar companies/other universities or deposit medium-quality ITO film here at Stanford. Acquiring the capability to produce high-quality ITO films would significantly help these solar research groups at Stanford by increasing the efficiency of their solar cells and/or reducing their cost of solar cell fabrication.

Also, it is recently shown [1] that ITO can be used as an interlayer in the low-resistance Metal-Interlayer-Semiconductor (MIS) contacts used in the Ge/Si transistors to achieve very low contact resistances, which is crucial for scaling down the technology nodes to 5 nm and beyond. In order to achieve very low contact resistances, ITO films with maximum carrier concentration and thus conductivity should be utilized. There is ongoing research at Stanford on this topic, aiming to build very low-resistance contact resistances for Si/Ge transistors. Providing this research with high-conductivity ITO films would be of noticeable significance.

The aim of this project is to come up with optimal sputtered ITO films for the two applications mentioned above, i.e. 1. ITO as transparent electrode in solar cells and 2. ITO as interlayer in low-resistance Metal-Interlayer-Semiconductor (MIS) contacts to be used in Si/Ge transistors. The first application requires 50-100 nm ITO films with maximum conductivity and transparency over the solar spectrum, simultaneously. Note that these two objectives could oppose each other, i.e. more carriers (conductivity) will cause more absorption and thus decrease optical transmission. We will investigate this in more details in the final result chapter. The second application requires 10-30 nm ITO films with maximum conductivity. We assume that ITO properties are uniform in the 10-100 nm range, meaning each recipe will result in the same conductivity and transparency properties when deposited in the 10-100 nm thickness range. With this assumption, we will focus our study on ITO films with thicknesses between 30-70 nm. Table 1 lists a summary of the motivation and the goal of the project.

Table 1. Project motivations and objectives

	Solar Application	**MIS Contact Application**
Usage	Transparent Electrode 	Interlayer in MIS contact 
Thickness	50-100 nm	10-30 nm
Parameters to optimize	1. Maximum conductivity (Carrier Concentration) 2. Maximum optical transmission over the solar spectrum (AM 1.5)	

4. Process Overview

The process mainly consists of two parts: 1. Sputtering of the ITO films using the Exfab sputtering tool, Lesker sputter (figure 1). 2. Physical and electrical characterization of deposited ITO films. The experiments are planned based on the Design of Experiments (DOE) method, using the JMP software package.

Figure 1. Lesker Sputter, the sputtering instrument in the Exfab facilities

We sputter ITO on a full glass (Pyrex) wafer with a quarter silicon wafer mounted on top of it, using Kapton tape (figure 2). The purpose of using the Kapton tape is to make a step on the surface of silicon and glass wafers, whose height will be equal to the thickness of the deposited ITO film. The silicon piece is used for thickness and stoichiometry measurement and the glass wafer is used for the rest of the measurements, mentioned in the next paragraph.

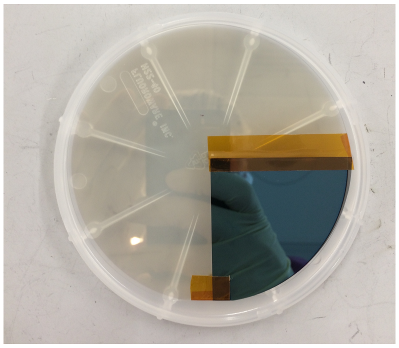


Figure 2. ITO is sputtered on a full glass (Pyrex) wafer with a quarter silicon wafer mounted on top of it, using Kapton tape.

The physical and electrical characterization of the ITO films includes the following experiments:

- Thickness measurement, using **Alphastep 500** profilometer in the SNF
- Sheet resistance measurement, using **Prometrix** 4-point probe in the SNF
- Optical transmission measurement, using **Jasco** spectrophotometer in the ExFab
- Stoichiometry measurement, using **PHI V3** XPS tool in the SNC

- Carrier concentration measurement, using the hall measurement tool in room Allen 152, supervised by some of the EE faculty.
    - The carrier concentration measurements are not presented in this report due to the reliability issues associated with them. According to multiple users of the tool, this Hall measurement tool is not reliable for the carrier concentration measurements of metal oxides, giving a random carrier concentration each time.

5. Design of Experiments (DOE)

At the Lesker sputtering tool, each sputtering recipe has 6 factors which fully define that recipe, assuming that all target locations result in the same deposition condition. These factors along with their operation range in this study are listed below.

1. Pressure (3-5 mTorr)
2. Power Mode (DC or RF)
3. Power (50-100 W)
4. O_2/Ar Ratio (0 – 0.05). Ar flow = 20 sccm.
5. Substrate Bias (0 - 50V)
6. Temperature (Room Temp. – 270 ^{o}C)

The purpose of this section is to find the parameters which are of significant effect on the conductivity and optical transmission values of the ITO films (the two responses of the DOE study). This process is called screening.

RF mode sputtering results in higher conductivity and optical transmission than the DC mode sputtering[2]. We therefore chose RF-sputtering over DC-sputtering. Also, since setting up the heating system and temperature in the Lesker sputtering tool is slightly time-consuming, we excluded it from the initial screening. This leaves us with four parameters (pressure, power, O_2/Ar ratio and substrate bias). Without using DOE we would have done $2^4 = 16$ experiments for the screening. Based on our DOE analysis we only need to do 5 experiments. However, in order to capture the 3rd order interactions among the factors, we decided to do 16/2 = 8 experiments.

Table 2 list the 8 screening experiments along their deposition rates, resistivity and absorption coefficient values. Note that the reported measurement values are in fact the average of the measurements done around the wafer. The standard deviation of the measurement was below 2% and 10% for the transmission and resistivity, respectively. It is easily seen in table 2 that O_2/Ar ratio hugely affects the conductivity of the film; even flowing a small amount of O_2 during the deposition significantly increases the resistivity. This is expected since the conductivity of the ITO films come from the oxygen vacancies. Therefore, more oxygen content will result in higher resistivity values and thus lower conductivity values. We also observe that higher deposition pressures result in higher resistivity values. Since the absorption coefficient values are close to one another, it is difficult to find out the significance of factors on the optical transmission only by looking at the results of table 2. Interestingly, the optimal recipes for conductivity and transmission are the same among these 8 experiments. This recipe is highlighted in the table.

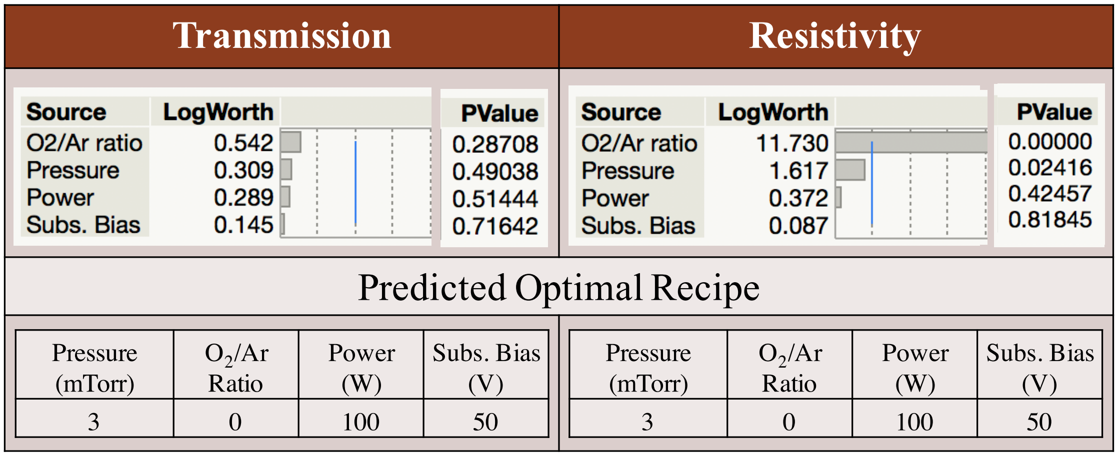
Table 2. The screening experiments, capturing the 3rd order interactions among the factors

Exp. #	Pressure (mTorr)	O_2/Ar Ratio	Power (W)	Subs. Bias (V)	Deposition Rate (nm/min)	Resistivity (ohm.cm)	Abs. Coeff. (1e4*cm^{-1})
1	5	0.05	100	50	0.82	8.67	6.57
2	5	0.05	50	50	0.43	7.48	7.42
3	5	0	100	0	2.50	2.3e-3	5.49
4	5	0	50	0	1.08	3.9e-3	6.57
5	3	0	100	0	1.78	7.2e-4	6.02
6	3	0	50	0	1.00	5.8e-4	4.98
7	3	0	100	50	1.53	4.8e-4	4.97
8	3	0	50	50	0.81	5.3e-4	5.49

Looking at experiment pairs 1-2, 3-4, 5-6 and 7-6 deposition rates, as expected, we observe that the deposition rates are approximately proportional to the power, which implies the stability of the plasma conditions among these experiments.

Table 3 shows the DOE analysis results of the 8 screening experiments along with the optimal conductivity and transmission recipes predicted. As can be seen in the table, O_2/Ar ratio and pressure with small p-values have significant effect on the resistivity, whereas power and substrate bias with p-values much higher than 0.01 have almost no effect on the resistivity.

Table 3. The DOE analysis performed on the 8 screening experiments shown in table 2



Transmission

Source	LogWorth	PValue
O2/Ar ratio	0.542	0.28708
Pressure	0.309	0.49038
Power	0.289	0.51444
Subs. Bias	0.145	0.71642

Resistivity

Source	LogWorth	PValue
O2/Ar ratio	11.730	0.00000
Pressure	1.617	0.02416
Power	0.372	0.42457
Subs. Bias	0.087	0.81845

Predicted Optimal Recipe

Pressure (mTorr)	O_2/Ar Ratio	Power (W)	Subs. Bias (V)
3	0	100	50

Pressure (mTorr)	O_2/Ar Ratio	Power (W)	Subs. Bias (V)
3	0	100	50

For the transmission, situation is different; all the factors have p-values much higher than 0.01, which implies that none of them are of important effect on the transmission and the transmission data has a semi-random distribution around all the factors. Therefore, the predicted optimal recipe for transmission is not reliable and it is a coincidence that the conductivity and transmission optimal recipes came out to be the same, as further verified in the next section on the repeatability of the depositions.

6. Repeatability Tests

In order to make sure the DOE analysis is reliable, we repeated 4 of the 8 screening experiments two more times to check the consistency of the measurement results. The results are shown in table 4 and 5.

Table 4. Repeatability Test on the Resistivity Data

Exp. #	Pressure (mTorr)	O_2/Ar Ratio	Power (W)	Subs. Bias (V)	Resistivity (ohm.cm)		
					1st Run	2nd Run	3rd Run
					Target 2	Target 1	Target 2
					Low Base Pressure	High Base Pressure	Low Base Pressure
2	5	0.05	50	50	7.48	13.2	N/A
4	5	0	50	0	3.9e-3	9.8e-03	3.52e-3
7	3	0	100	50	4.8e-4	1.75e-03	6.42e-4
8	3	0	50	50	5.3e-4	1.82e-03	8.45e-4

As can be seen in table 4, the resistivity measurement results are consistent among the three runs. Note that run 2 was done at a much higher base pressure (right after opening/closing the deposition chamber). Also, it was done with ITO target installed on a different target location than run 1 and 3. These two factors, particularly the first one, has caused the resistivity to increase by a factor of ~2-4. However, since the data is consistent among all three runs, the conclusion is that the resistivity data is repeatable.

Table 5. Repeatability Test on the Optical Transmission Data

Exp. #	Pressure (mTorr)	O_2/Ar Ratio	Power (W)	Subs. Bias (V)	Abs. Coefficient ($1e4*cm^{-1}$)		
					1st Run	2nd Run	3rd Run
					Target 2	Target 1	Target 2
					Low Base Pressure	High Base Pressure	Low Base Pressure
2	5	0.05	50	50	7.42	6.98	N/A
4	5	0	50	0	6.57	4.58	7.20
7	3	0	100	50	4.97	4.64	7.90
8	3	0	50	50	5.49	8.30	5.08

Looking at table 5, we observe that the transmission data are consistent among the first two runs but not among the three. This was not unexpected from the semi-randomness nature of the transmission data demonstrated by the high p-values of all factors in the transmission DOE analysis. The conclusion would be that the transmission data is not completely repeatable. We base our decision on runs 1 and 2 and use the predicted optimal recipe suggested by the JMP DOE analysis shown in table 3 and fine-tune that recipe by individually varying the factors of the recipe around the optimal values. The results are presented in the following chapter.

7. Final Results

In this section, we study the effect of individually varying the 5 knobs of the sputtering system, i.e. the pressure, power, O_2/Ar ratio, substrate bias and the temperature, around the predicted optimal transmission and resistivity recipe – 100W power, 3 mTorr pressure, 50V substrate bias, zero O_2/Ar ratio with no heating (70 ^{o}C), to 1. Find out how they change the resistivity and transmission and 2. Fine-tune the optimal recipe.

7.1. Pressure

As observed in figure 3, the resistivity minimum is at 3 mTorr (predicted optimal recipe). Looking at the compositional data, the decrease in the resistivity can be attributed to the increase in the tin content of the ITO.

Figure 3 shows that the transmission increases as the pressure is increased, with a minimum at 5 mTorr. Note that the predicted optimal recipe was at 3 mTorr. The difference between the absorption coefficients of 3 and 5 mTorr pressure are small, resulting in essentially the same transmission in 30-100 nm ITO films. Also, given the high p-values in the DOE analysis, this result might change when repeated. Therefore, we keep 3 mTorr as the pressure of our optimal recipe. The transmission data can be correlated to the oxygen content of the ITO; the more the oxygen content, the smaller the absorption coefficient and the more the optical transmission.

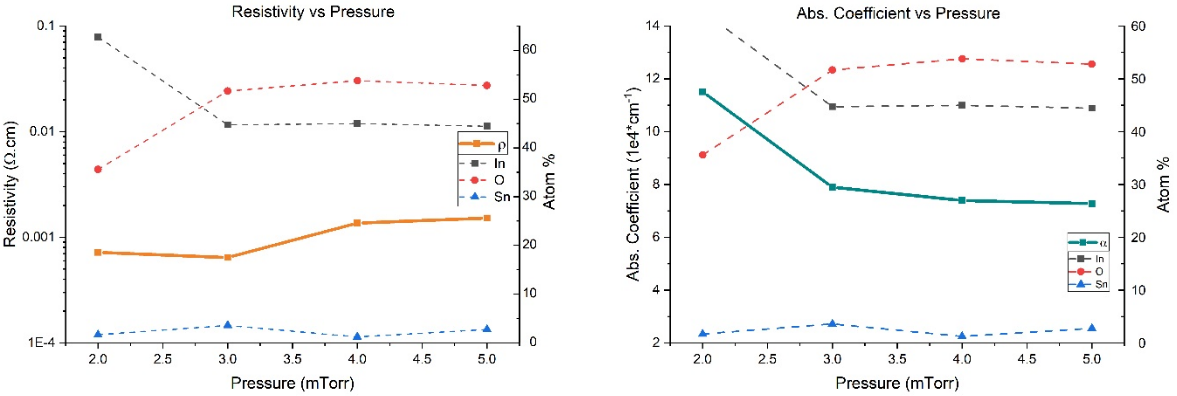


Figure 3. Resistivity Vs. pressure (left) and absorption coefficient Vs. pressure (right)

7.2. O_2/Ar ratio

As can be seen in figure 4, increasing the O_2/Ar ratio drastically increases the resistivity. Minimum resistivity is achieved when no oxygen is flown during the deposition (predicted optimal recipe). This is explained by the fact that the conductivity of ITO comes from the oxygen vacancies, making oxygen-rich ITOs very resistive. No specific correlation is seen between the resistivity values and the compositions of the ITO films. It is surprising that the oxygen content of the experiment with zero oxygen is higher than the one with 0.025 O_2/Ar. This can be attributed to inaccuracies in the XPS measurement.

Figure 4 shows that the absorption coefficient is maximized – the optical transmission is minimized - at 0.025 O_2/Ar. The predicted recipe with zero oxygen shows the best optical transmission properties. Same as the pressure trend, the transmission data can be correlated to the oxygen content of the ITO, with more oxygen causing more transmission over the solar spectrum.

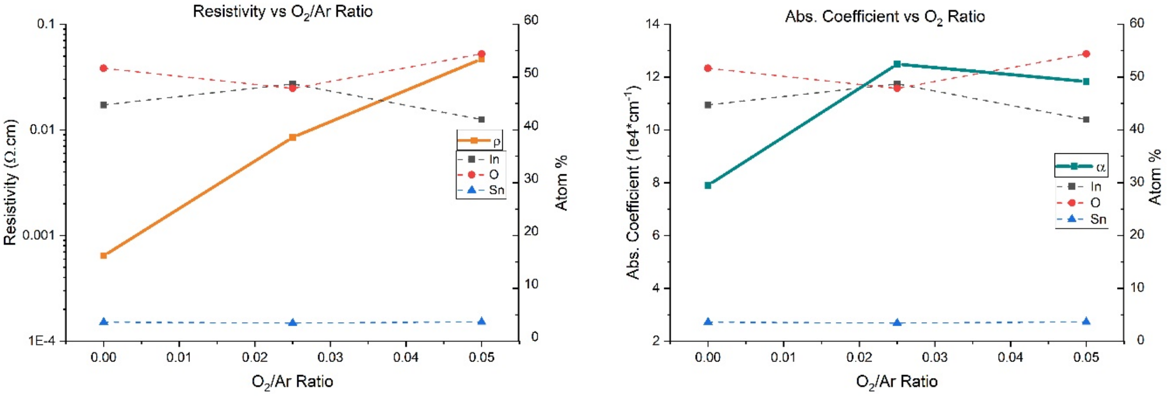


Figure 4. Resistivity Vs. O_2/Ar ratio (left) and absorption coefficient Vs. O_2/Ar ratio (right)

7.3. Power

Looking at figure 5, the power does not have a significant effect on the resistivity values, as expected from the high p-value of power in the DOE analysis. The predicted optimal recipe achieves the lowest resistivity. The resistivity values are inversely proportional to the tin content of the ITO films, as seen in the resistivity Vs. power results.

The transmission is maximized at 75W, with a small difference with the absorption coefficient of the predicted optimal recipe. With the same discussion as the one in section 6.2, we keep 50W as the optimal power value for the transmission recipe. This time the transmission data cannot be correlated with the oxygen content of the ITO films.

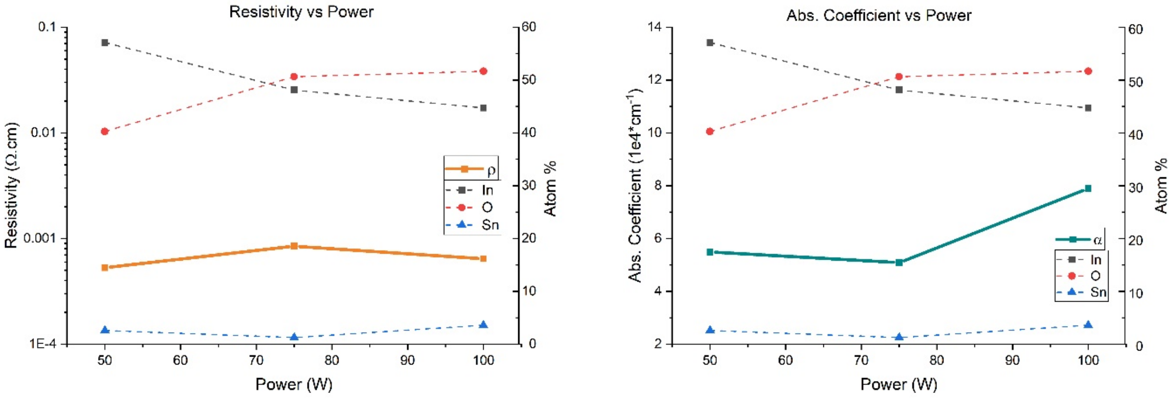


Figure 5. Resistivity Vs. power (left) and absorption coefficient Vs. power (right)

7.4. Substrate Bias

As expected from the high p-value of substrate bias in the resistivity DOE analysis, figure 6 demonstrates that the effect of substrate bias on the resistivity is very insignificant. The predicted optimal recipe has the lowest resistivity values. The resistivity values are correlated with the tin content of the ITO films; ITOs with higher tin content are more conductive.

There are no specific trends in the transmission data. Nevertheless, the predicted optimal recipe achieves the highest transmission. The transmission data cannot be correlated with the XPS measurements.

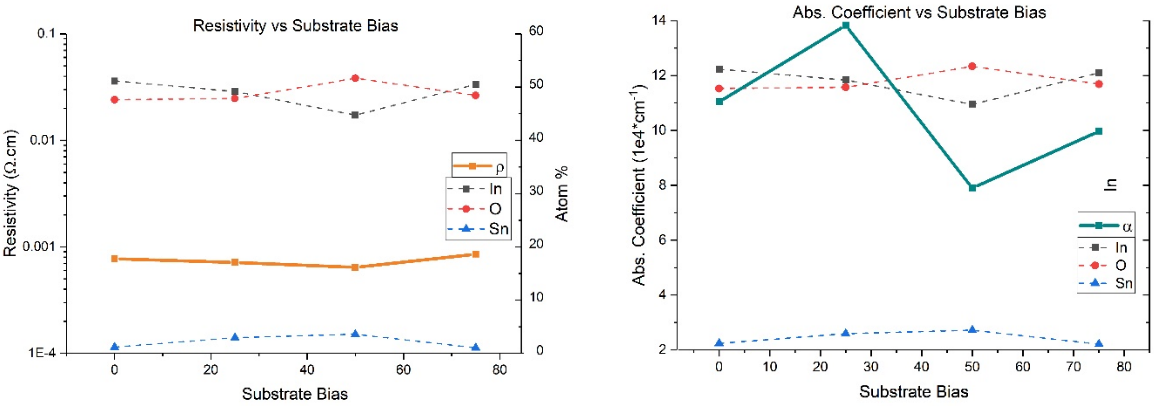


Figure 6. Resistivity Vs. substrate bias (left) and absorption coefficient Vs. substrate bias (right)

7.5. Temperature

Figure 7 shows that increasing temperature slightly increases the resistivity, keeping the case with no heating as the optimal recipe. The increase in resistivity can be attributed to the decrease in the tin content.

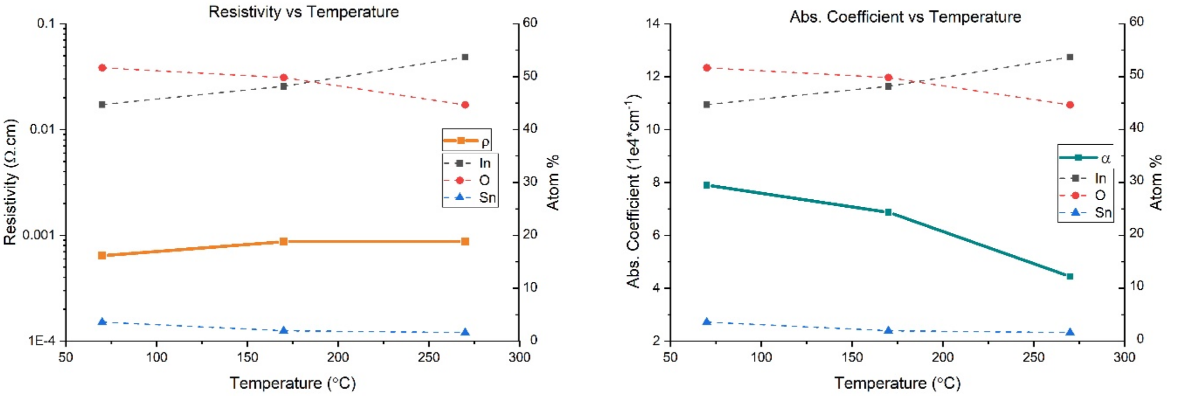


Figure 7. Resistivity Vs. temperature (left) and absorption coefficient Vs. temperature (right)

As observed in figure 7, transmission is significantly increased by increasing the temperature, making the optimal transmission receipe happen at 270 ^{o}C. This can be attributed to the annealing effect which reorders the atoms and thus improves the transmission. Inspired by this transmission boost due to temperature increase, we did another deposition at 400 ^{o}C, however, the Kapton tape used on the sample was burnt during the deposition making it impossible to measure thickness of the ITO film. Using baked photo-resist instead of Kapton tape would resolve this issue. We recommend the reader to try that recipe if interested in highly-transparent, highly-conductive ITO films.

8. Conclusion

Given the results shown in the previous section, the optimal resistivity and transmission recipes are as follow (table 6):

Table 6. The optimal resistivity and transmission recipes of sputtered ITO fabricated by Lesker Sputter

Optimal Resistivity Recipe	
O_2/Ar Ratio	0
Pressure	3 mTorr
Power	100 W
Subs. Bias	50 V
Temperature	~ 70 ^{o}C (no heating)
Resistivity	4.8e-4 ohm.cm

Optimal Transmission Recipe	
O_2/Ar Ratio	0
Pressure	3 mTorr
Power	100 W
Subs. Bias	50 V
Temperature	270 ^{o}C
Abs. Coeff.	44400 cm^{-1}

Given its absorption coefficient value, the optimal transmission recipe results in 80% transparency over the solar spectrum for a 50 nm ITO film, which is pretty high compared to the ITO films used in the industry and academic research. [2]

The trends presented in the previous chapter also demonstrated that in general the more the tin content and the less the oxygen content of an ITO film, the more conductive it is. Also, more oxygen also generally results in higher optical transmission over the solar spectrum. Heating anneals the ITO films, further improving their optical transmission.

9. Acknowledgement

We would like to most sincerely thank the E 241 teaching staff, mentors and students, the SNF staff and our mentors for their invaluable help and support throughout this project.

10. References

[1] P.P. Manik, S. Lodha “Contacts on n-type germanium using variably doped zinc oxide and highly doped indium tin oxide interfacial layers” *Appl. Phys. Express*, 8 (5) (2015), p. 051302,
[2] Ocal Tuna *et al* 2010 *J. Phys. D: Appl. Phys.* **43** 055402

11. Appendix: XPS Study of ITO Thin Films

The chemical stoichiometry of the deposited ITO thin films was assessed by X-ray photoelectron spectroscopy (XPS). XPS analysis is an effective way to evaluate the quality of the film. The XPS analysis was performed with an XPS: PHI Versaprobe 3, (ULVAC-PHI, INC, Japan) The samples were analyzed using a ULVAC-PHI charge neutralizer system. The elemental and chemical-stoichiometry spectra were collected using the High-Power setting with a beam spot of roughly 1400 x 300um. The typical measurement depth is between 10 and 50 Å. The spectrometer is a mono-chromatized Al(Kα) Source; Vacuum ~ $1.2 \times 10^{(-7)}$ Pa. All the XPS surveys and high-resolution spectra of the In $3d^5$, O $1s^1$ and Sn $3d^5$ binding energy regions were collected at pass energies of 117.4eV and 23.5 eV, respectively. The XPS high resolution peaks of the In $3d^5$, O $1s^1$ and Sn $3d^5$ for all samples are shown in Figure I and II.

The O $1s^1$ spectra has been fitted with two peaks located at a binding energy of 530.5 eV and 531.8 eV. The Sn $3d^5$ spectra with a peak at 486.8 eV and 488.0 eV, and the In $3d^5$ at 444.9 eV and 446.0 eV; as seen in table A. The peaks have been labelled as to distinguish them during discussion. The peak positions and reference binding energy values of the atoms of interest is presented in Table I. The binding energy scale was calibrated using the C 1s peak at 284.8 eV. Furthermore, to obtain accuracy in our atom percentage proportions we did a peak fitting of the O $1s^1$ curve taking the peak 530.5 as the Indium Oxide main component, and the peak of 532.6, normally associated with carbon oxides as well as indium oxides.

Table I. Binding energy values for non-interfacial ITO [1]

Composition	**In $3d^{5/2}$ (eV)**	**O $1s^1$ (eV)**	**Sn $3d^{5/2}$ (eV)**
ITO	444.6	530.5	486.4
ITO-a	444.5	531.4	
In(OH)x	446.0	532.6	
SnO_2		530.6	487.1

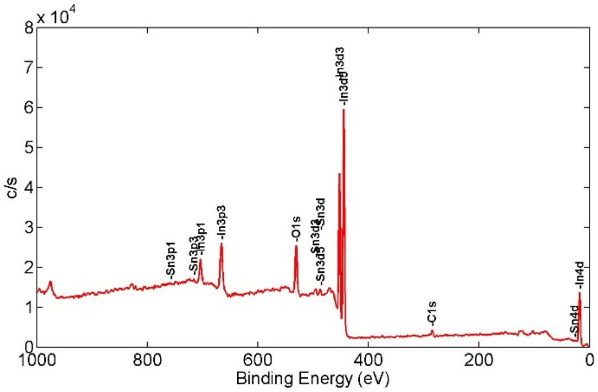


Fig. I Indium Tin Oxide XPS spectra of survey

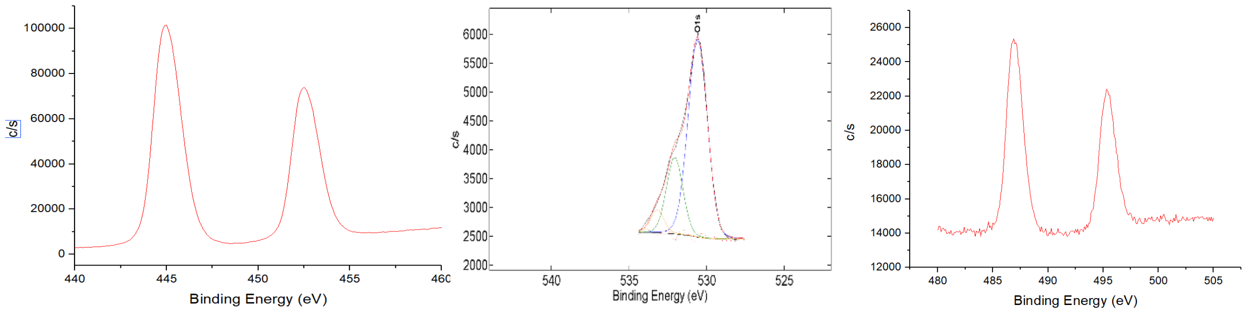


Fig. II Indium Tin Oxide XPS spectra of A) In 3d$^{5/2}$ B) O 1s ^{1} and deconvolution, and C) Sn 3d $^{5/2}$ of the as deposited bulk sample.

In order to judge the repeatability of our samples we ran 3 sets of samples with the same parameters. Fig. III presents the high-Resolution spectra for the sample with 100 W power, 5 mTorr pressure, 50 V substrate bias and no oxygen (top green) and several of our 100 W, 3 mTorr, selected in the study as parameters of our lowest resistivity recipe. All the samples with 100 W power and 3 mTorr pressure present almost identical spectra for the oxygen atom making this atom the one that presented the most change along all our samples.

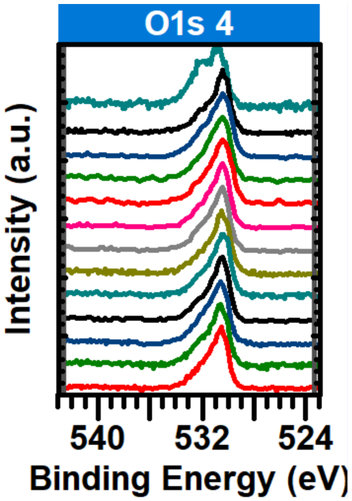


Fig. III Elemental composition of the oxygen atom trough several samples.