E241 Spring 2022 ALD ITO Report

Shuhan Liu[1], Xinyi Wen[1], Nathalie Moreno[2]
Mentors: Vijay Narasimhan[3], Graham J. Ewing[4], Michelle Rincon[5], Angelica Zacatzi[3], H.-S. Philip Wong[1]
[1] Department of Electrical Engineering, Stanford University
[2] EE Research Experiences for Undergraduates Program, Stanford University
[3] EMD Performance Materials
[4] Stanford Nanofabrication Facility, Stanford University
[5] Onsemi

1. Motivation

ITO is a conducting and transparent material widely used for electrodes in many applications like transistors, batteries, and optical devices. The common method to deposit ITO is sputtering, but sputtered ITO tends to be rough, non-uniform, and non-conformal. Besides, the ITO composition is pre-defined by the sputtered target and has little tunability for different needs. ALD (atomic layer deposition) is a deposition method generally better than sputtering in roughness, conformality, and uniformity, as well as having better control in thickness and composition. Therefore, in this project, we aim to develop an ALD process for ITO using two tools: Fiji2 in SNF and Fiji4 in Prof. Philip Wong's Allen Annex laboratory. ALD of ITO in Fiji4 will be available to the SNF labmember community.

2. Methods

The full name of ITO is Indium Tin Oxide, which consists of Indium oxide and Tin oxide, so the ALD growth for ITO is to deposit supercycles of In_2O_3 and SnO_2 (Fig. 0). That is, the ALD ITO recipe has three loops: to deposit m cycles of In_2O_3, and then to deposit n cycles of SnO_2 (typically n = 1), and repeat this supercycle loop for p times. To develop ALD ITO recipe, In_2O_3 recipe and SnO_2 recipe should be developed first. There is already a well-developed recipe for SnO_2 in SNF, but not for In_2O_3, so our first task is to develop a In_2O_3 recipe.

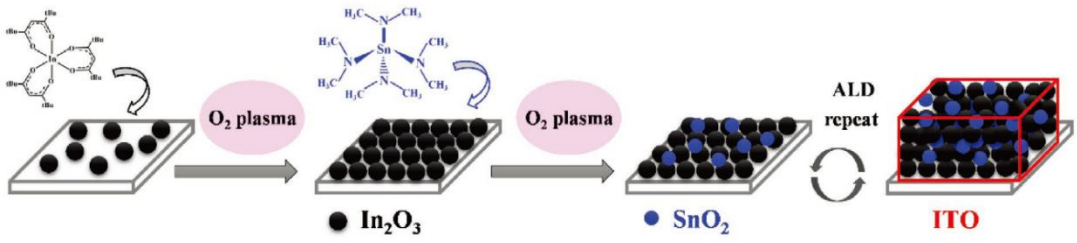

Figure 0. ALD ITO process flow with supercycles of In_2O_3 and SnO_2 from [9]

From a literature review, we found that there are two kinds of In precursor that

may suit our needs: indium cyclopentadienyl (InCp) and trimethylindium (TMIn). TMIn is more attractive than InCp with higher vapor pressure and lower cost [1], but InCp is the currently used In precursor in SNF. It took five weeks to place the order and deliver TMIn. (TMIn bottle arrived this fast only through the efforts of Vijay and Angelica at EMD Performance Materials.) As for the ALD tools, Fiji2 is the SNF tool to deposit conducting material, but a shared tool is usually not so stable. Fiji4 is an ALD tool in Prof. Philip Wong's lab but has been down for years, so it took some time for Fiji4 to come back to life in the first few weeks of the quarter. (It only came up due to the hard work of Carsen and Graham.)

Therefore, in this project, during the first-half quarter, we used InCp precursor and Fiji2 to develop In_2O_3 and ITO. During the second-half quarter, we developed In_2O_3 and ITO with TMIn precursor and Fiji4.

ALD films were grown on two types of insulating substrates, glass wafer and Si (100) wafer with 100nm thermal SiO_2 on top. One ALD cycle is a sequence of precursor pulse time (t1), precursor purge time (t2), O_2 plasma pulse time (t3), and O_2 purge time (t4). The timing sequence is expressed as t1-t2-t3-t4 in this report.

For In_2O_3, we went through a standard ALD development process to develop the In_2O_3 recipe:

a. Pick a substrate temperature that you expect in the ALD window of the precursor from the literature. Select an 80-100 cycle process so you can easily measure your film. (Aim for about 8-10 nm)
b. Run a process with long-ish dose times and then get your precursor temperature locked in. (Precursor temperature)
c. Fix the oxygen plasma time at some high value, then sweep the precursor dose from low to high values. You are looking for a transition from non-uniform growth to something more stable. Set your precursor dose to a stable level. (Saturation curve for precursor).
d. Fix the precursor dose at the saturated value you found before, and then sweep the oxygen plasma time from low to high values. You are looking for a transition from non-uniform growth to something more stable. Set your reactant dose to a stable level. (Saturation curve for oxygen).

After that, we used the well-developed In_2O_3 and SnO_2 recipes for the ITO recipe. The ternary ALD ITO film was fabricated at a common temperature using a mixture of In_2O_3-SnO_2, wherein binary In_2O_3 and SnO_2 cycles are deposited repeatedly in "supercycles". The ratio of component oxides can be controlled by changing the number of In_2O_3 and SnO_2 cycles in one supercycle. The recipe is described as:

(m-cycle In_2O_3 + 1-cycle SnO_2) * n-supercycle

where n is the number of ALD supercycles and m is In_2O_3 to SnO_2 ratio in one ITO supercycle. A series of ALD ITO films were deposited on the planar SiO_2/Si substrate and glass wafer with different n and m. By changing the In:Sn cycle ratio m, we can find the ITO composition with lowest resistivity.

3. Results for In_2O_3 and ITO with InCp precursor by Fiji2

3.1 In_2O_3 with InCp precursor by Fiji2

a. The substrate temperature was set to 225℃ because the SnO_2 recipe uses 225℃ as the substrate temperature. This temperature is also in the ALD window according to [2].

b. We tested the precursor temperature of 75℃, 100℃, 125℃, and 150℃. The results are shown in Table 1. The Fiji2 pressure pulse can indicate the successful deposition In_2O_3 of but not necessary, so we further tested XPS. The lowest precursor temperature to get In_2O_3 deposition is 125℃, and there is a concern for decomposition at 150℃, so we locked the precursor temperature to 125℃. (2023/3 Update: For a new InCp bottle, the precursor temperature is tested to be 60C)

Precursor temperature	75℃	100℃	125℃	150℃
Pressure pulse	No	No	No	Yes
XPS In peak	No	No	Yes	Yes

Table 1 XPS of Fiji2 In_2O_3

c. The result of the precursor dose test is shown in Figure 1. The film thickness was measured by Woollam M2000 spectroscopic ellipsometer. We expected to obtain the saturation trend but didn't, and we think it's probably because the saturation trend is overwhelmed by variation and randomness due to shared tool Fiji2, even if we did chamber seasoning before each run.

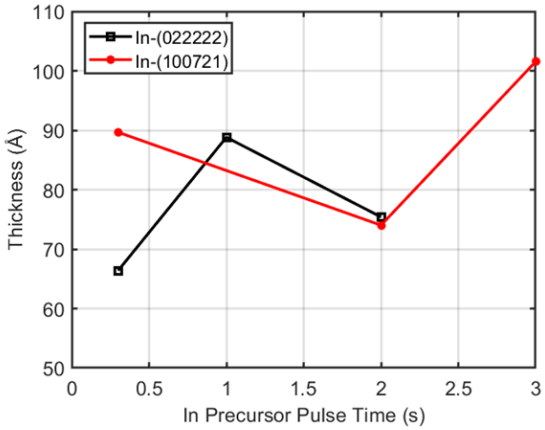

Figure 1 Saturation curve of Fiji2 In_2O_3.

3.2 ITO with InCp precursor by Fiji2

a. Resistivity

To extract the electrical characteristics of the ITO films, sheet resistance

(Ω/sq.) was measured by Eddycurrent LEI1500 contactless sheet resistance system. The film resistivity (Ω·cm) can be calculated by multiplying the sheet resistance by the film thickness. The resistivity for different ITO compositions is shown in Figure 2. Resistivity reaches the minimum value of 5.8 x 10^{-4} Ωcm when In:Sn cycle was set to 39. As a reference, the minimum resistivity of ITO deposited by Lesker is 4.8 x 10^{-4} Ωcm according to the previous E241 project report [3]. And all the resistivity values for our ALD samples fall into the normal range of ITO resistivity.

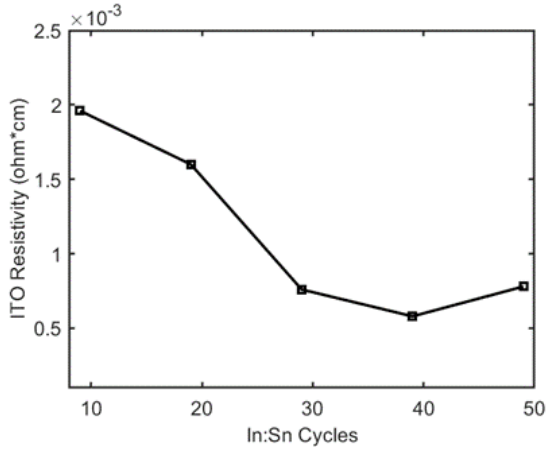

Figure 2 ITO film resistivity versus In_2O_3: SnO_2 cycle ratios in one supercycle for Fiji2 ITO.

b. Growth rate

Similar to In_2O_3, the growth rate of ITO was not very stable, as shown in Figure 3. It may also come from the composition difference, but we think the growth rate variation is more related to the share tool with different chamber conditions for each run. (Note: some SNF labmembers used our recipe to repeat the runs consecutively, and got very stable growth rate even for different In : Sn cycles.)

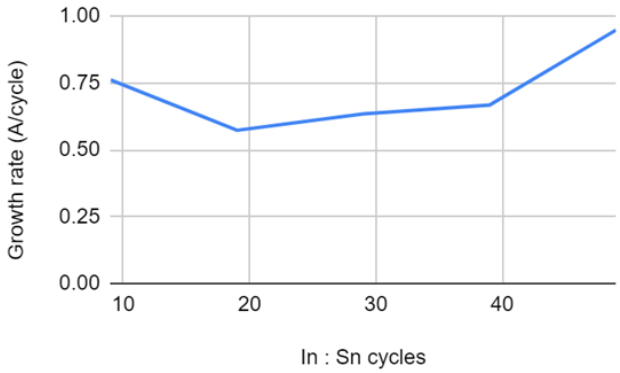

Figure 3 Growth rate of Fiji2 ITO.

c. XPS (X-ray photoelectron spectroscopy)

After deposition, PHI VersaProbe 3 in SNSF was used to acquire XPS data for determining the elemental composition of the film. It used Al (Ka)

radiation (1486 eV) as an excitation source. Both survey and high-resolution scans were conducted. The composition (XPS In:Sn ratio) curve for different ALD In:Sn cycle ratios is shown in Figure 4, from which we can see that the actual In:Sn ratio for the ALD film is much less than the set In:Sn cycle ratio. The result in [2] also shows a similar trend with more Sn than expected. After discussing with Prof. Ted Kamins, we think the reason is different surface absorption and coverage of In and Sn atoms.

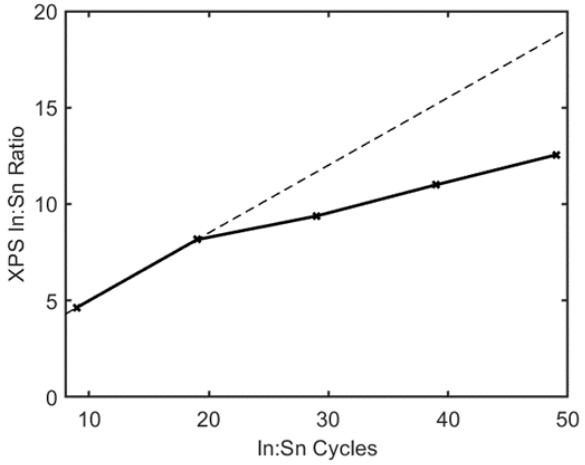

Figure 4 XPS In:Sn ratio versus In_2O_3: SnO_2 cycle ratios in one supercycle for Fiji2 ITO.

4. Results for In_2O_3 and ITO with TMIn precursor by Fiji4

4.1 In_2O_3 with TMIn precursor by Fiji4

Similar to the general process of ITO film deposition by Fiji2, the first step was to develop an optimized ALD In_2O_3 recipe using Trimethylindium (TMIn) on Fiji4 by finding the thickness saturation curves with respect to In precursor pulse time and the plasma pulse time. Fiji4 (Cambridge NanoTech Fiji F200 series) is an ALD tool owned by Prof. Philip Wong's lab, capable to accommodate wafer sizes up to 8-inch (Note: 4-inch wafer would be recommended to get better uniformity). The substrate temperature was set to 200°C, which is in a common ALD temperature window for In_2O_3. To date, [4-7] have reported successful ALD In_2O_3 using TMIn precursor at this temperature.

a. TMIn precursor temperature

   To decide the ampoule temperature of the TMIn precursor used in Fiji4 In_2O_3, two samples were grown with TMIn temperature at 30°C and 40°C separately. The timing sequence was 0.5s-5s-15s-15s. After film deposition, the composition of the two In_2O_3 samples was measured using the PHI XPS tool in SNSF. The XPS results including the atomic concentration of oxygen, indium, and carbon are shown in Figure 5.

The elemental composition and film thickness are very close at the TMIN ampoule temperature of 30℃ and 40℃. As suggested by our mentors and the TMIn precursor providers Dr. Vijay Narasimhan and Dr. Ravi Kanjolia, the manifold and delivery line temperature should be 20℃ above the precursor temperature. Considering that the optimized Sn precursor temperature is 60℃, and In and Sn precursors share the same manifold and delivery line temperature for the Fiji ALD, we chose 40℃ as the ampoule temperature of the TMIn precursor for both In_2O_3 and ITO film deposition.

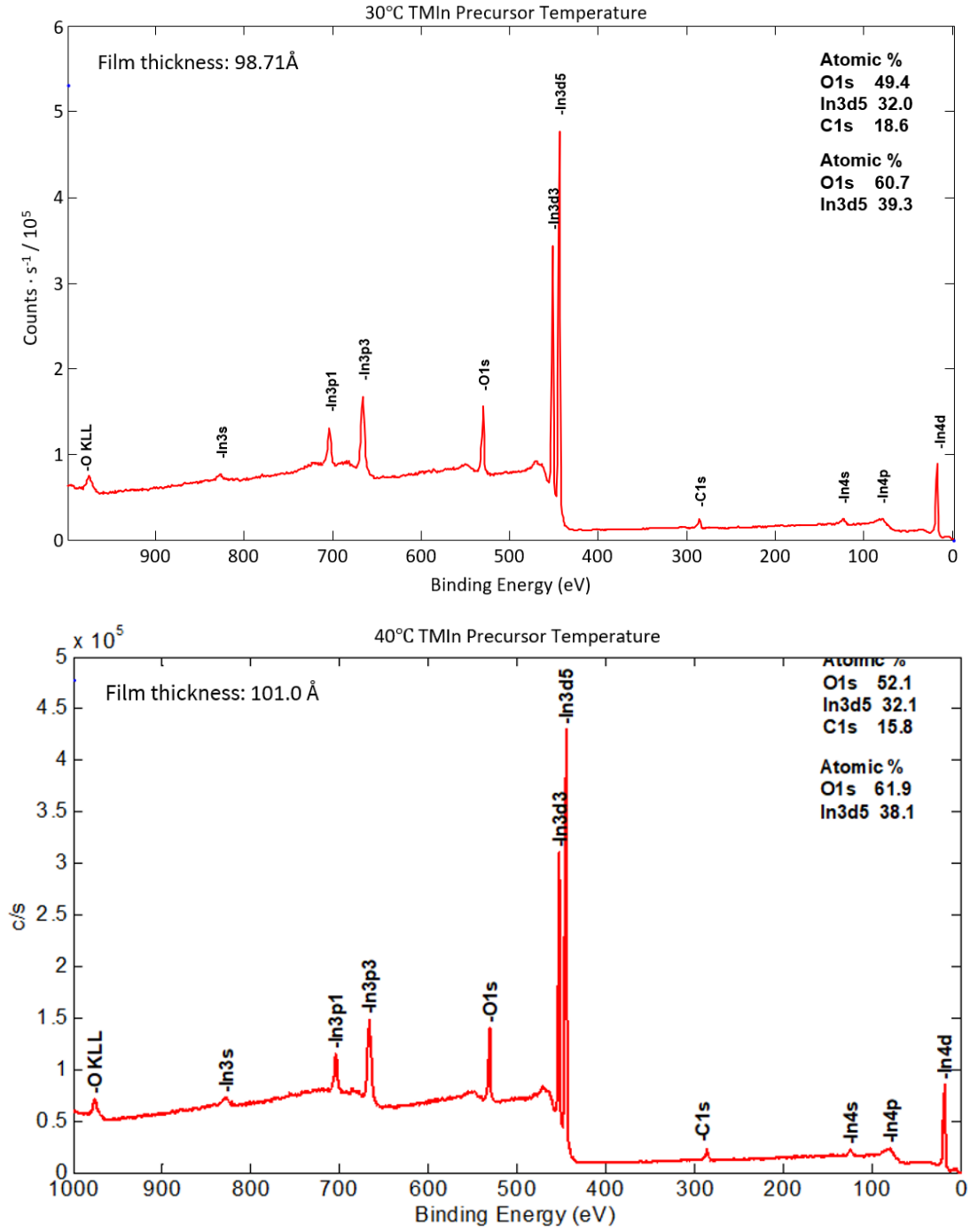

Figure 5 XPS survey spectra of Fiji4 In_2O_3 at 30℃ and 40℃.

b. Saturation curves of In dose and O_2 plasma pulse time

The saturation curves of In_2O_3 with respect to In dose and O_2 plasma pulse time are shown in Figure 6. The oxygen mass flow rate was 20sccm and the RF plasma power was 300W. When developing the saturation curve of In precursor pulse time, the precursor purge time was 5s, and O_2 plasma time was 15s.

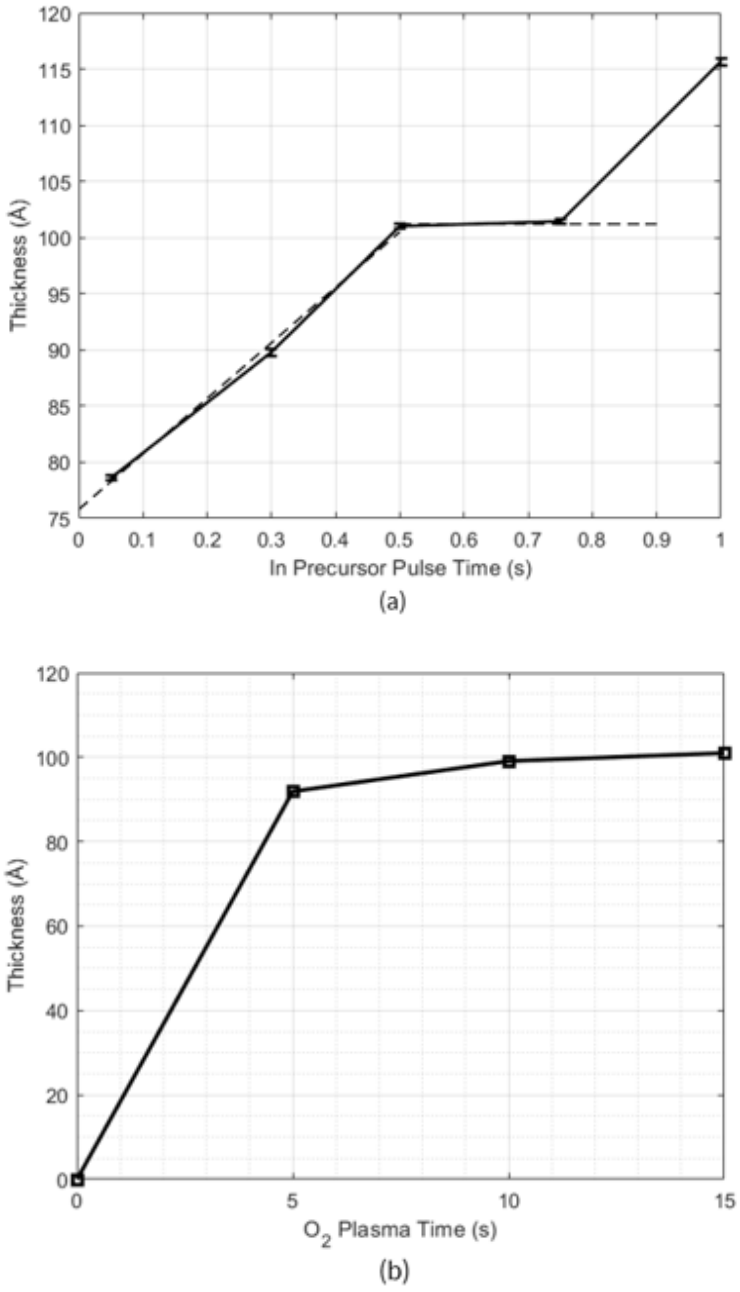

Figure 6 Fiji4 In_2O_3 saturation curves

As Figure 6 (a) shows, In_2O_3 thickness saturates when In precursor pulse time is 0.5s. The extremely high thickness at 1s In dose is probably due to

the CVD effect. As we overdose In precursor, it cannot be fully pulled out of the chamber atmosphere before the plasma starts. In that case, reactions happen in the gas phase as well as surface reactions, leading to more products on the wafer and thus higher film thickness.

After determining the In precursor pulse time of 0.5s, we developed the saturation curve of O_2 plasma pulse time in the same manner. As Figure 6 (b) shows, In_2O_3 film thickness saturates when the O_2 plasma pulse time is 10s. Therefore, the optimized timing sequence of the In_2O_3 recipe is 0.5s-5s-10s-10s, and the corresponding growth rate per cycle (GPC) is 1.24 Å/cycle for this recipe.

4.2 ITO with TMIn precursor by Fiji4

a. SnO_2 with TDMA-Sn precursor by Fiji4

We used the same Fiji2 SnO_2 recipe with TDMA-Sn precursor and deposited 80 cycles of SnO_2 on Fiji4 for film characterization. The timing sequence of this recipe is 2s-10s-10s-10s, and the GPC is 0.95 Å/cycle. The XPS data revealed the presence of Sn, O, and C, which is shown in Figure 7.

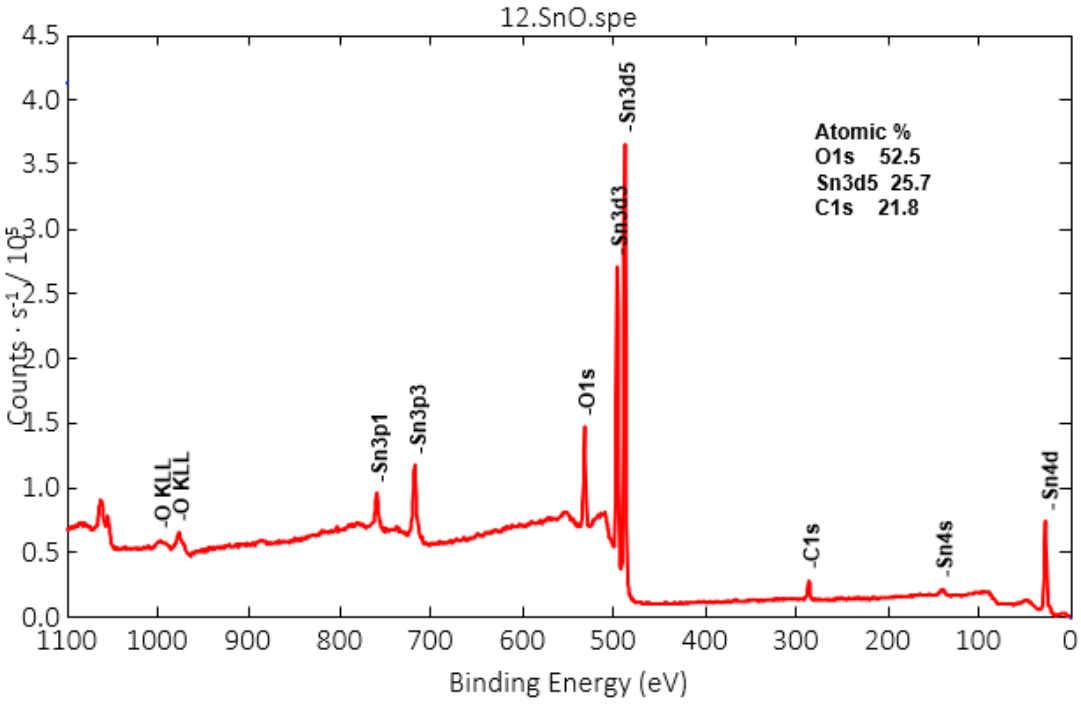

Figure 7 XPS survey spectra of ALD SnO_2 on Fiji4.

b. Growth rate

The ITO growth rate for Fiji4 ITO is calculated by growing a series of ITO samples at different ALD total cycles. The GPC at In:Sn ratio m=9 and 19 are extracted in Figure 8. The GPC is 1.19 Å/cycle when m=9 and 1.14 Å/cycle when m=19.

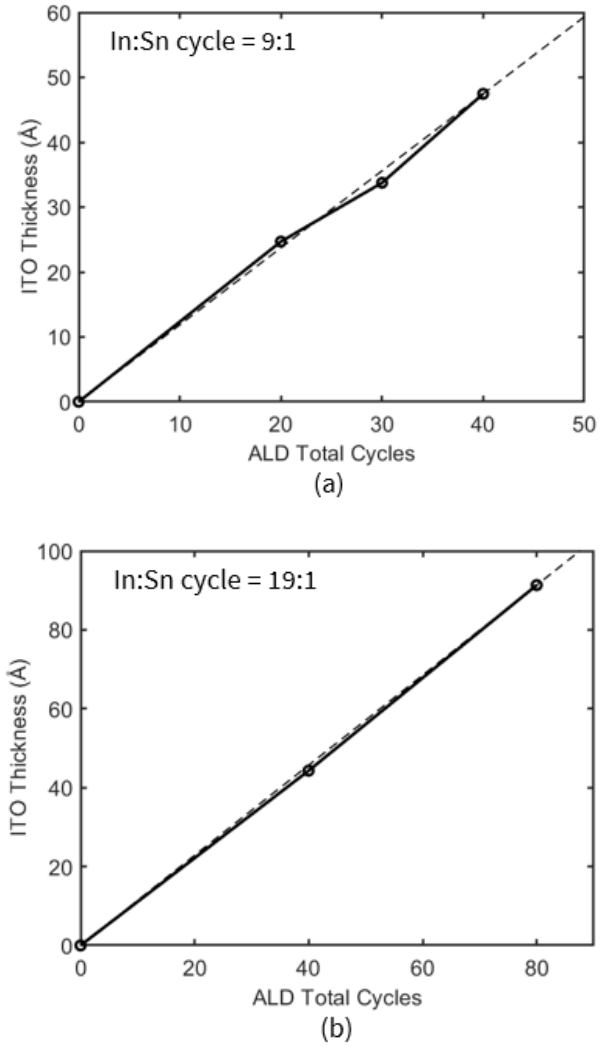

Figure 8 ITO thickness vs. ALD total cycles at different In:Sn cycles.

c. XPS

The elemental composition of In and Sn of the ITO films were measured using XPS at different ALD In:Sn ratio m, as shown in Figure 9. Similar to Fiji2 ITO, the actual In composition of Fiji4 ITO from XPS measurements is lower than m, the In_2O_3: SnO_2 cycle ratio in one supercycle. This implies that the In_2O_3 deposition is suppressed by the preceding SnO_2 ALD cycle, which has been reported in [8]. At a given In_2O_3: SnO_2 cycle ratio in one supercycle, the In content percentage in Fiji4 is lower than that in Fiji2.

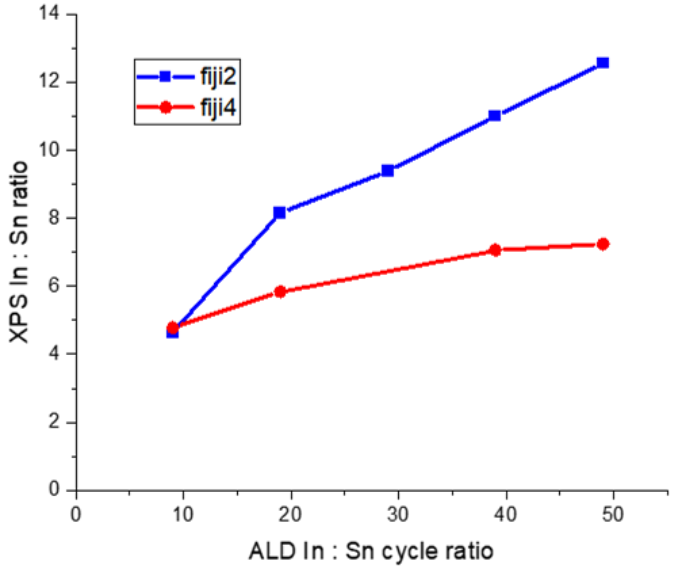

Figure 9 XPS In:Sn ratio versus In_2O_3: SnO_2 cycle ratios in one supercycle.

To further improve XPS In:Sn ratio in Fiji4 ITO films, we tried several methods including decreasing substrate temperature, reducing Sn precursor pulse time, and reducing O_2 plasma time. In this series of experiments, the In precursor pulse temperature and purge temperature were 0.5s and 5s respectively, m=19, and n=4. The O_2 plasma purge time was the same as the O_2 plasma pulse time. The results are shown in Table 2, and In composition can be enhanced in these three ways. However, the ITO film resistivity of sample #2-4 was still higher than $3\times 10^{-3}\Omega\cdot$cm.

Sample #	Substrate temp (°C)	Sn pulse time (s)	O_2 plasma time (s)	XPS In:Sn
1	200	2	10	5.84
2	150	2	10	7.11
3	200	1	10	6.20
4	200	2	5	6.33

Table 2 Fiji4 ITO XPS In:Sn at different substrate temperatures, Sn pulse time, and O_2 plasma time.

d. Resistivity

The lowest resistivity of Fiji4 ITO is $3\times 10^{-3}\Omega\cdot$cm when m=19, which is about five times higher than the resistivity of Fiji2 ITO. The resistivity of the other samples is too high to be measured due to the upper bound limit of Eddycurrent measurement system.

5. To improve the resistivity of ITO with TMIn precursor by Fiji4

As a follow-up project, Nathalie Moreno from EE REU program mentored by Shuhan Liu, continued this work to improve the resistivity of ITO with TMIn

precursor by Fiji4.

Firstly, to better understand reasons of the high resistivity of ITO with TMIn precursor by Fiji4, we installed InCp precursor on Fiji4 and made some ITO samples with Fiji4 InCp precursor. The growth rate of Fiji4 InCp ITO samples (1.56 ~ 1.67 A/s) are higher and more stable than the counterparts in Fiji2. However, the resistivity of Fiji4 InCp ITO samples ($4\times 10^{-3}\Omega\cdot$cm ~ $8\times 10^{-3}\Omega\cdot$cm) is higher than Fiji2 ones. But this resistivity is still lower than most of the TMIn ITO samples. Therefore, from this control experiments, we can draw the conclusions that the reason of high resistivity of ITO with TMIn precursor by Fiji4 is both from the precursor and tool: ITO with InCp precursor has lower resistivity than ITO with TMIn precursor; and ITO deposited by Fiji2 has lower resistivity than ITO deposited by Fiji4.

To improve the resistivity of ITO with TMIn precursor by Fiji4, we firstly tried different In : Sn cycle, while keeping the thickness constantly at ~13nm and deposition temperature at 200C. Note that for previous experiments, we always kept the Sn cycle number to be 1 in a supercycle, but here for further exploration we released that constraint and tried some other combinations (Table 3). After trying 14 samples, the growth rate is still stable at 1.28 ± 0.04 Å/ cycle (Figure 10). And the lowest resistivity is achieved by In : Sn cycle of 27: 3 (27-cycle In_2O_3 and 3-cycle SnO_2 in one supercycle), which is $6\times 10^{-3}\Omega\cdot$cm.

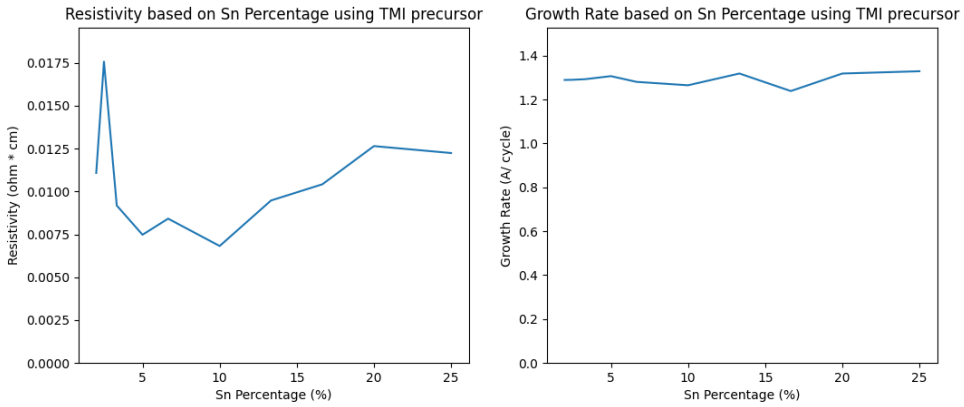

Figure 10 Resistivity and growth rate of ITO samples with different In : Sn cycle

Sample #	In : Sn cycle ratio	Thickness (A)	Growth Rate (A/cycle)	Sheet resistance (ohm/sq)	Resistivity (ohm*cm)	Deposition Temp
1	19:1	129.11	1.29	6094	0.0079	200C
2	19:1	130.65	1.31	5723	0.0075	200C
3	29:1	155.11	1.29	5919	0.0092	200C
4	49:1	128.91	1.29	8594	0.0111	200C
5	39:1	154.78	1.29	11349	0.0176	200C
6	25:5	148.63	1.24	7010	0.0104	200C
7	15:5	132.88	1.33	9211	0.0122	200C
8	24:6	158.21	1.32	7992	0.0126	200C
9	26:4	158.22	1.32	5988	0.0095	200C
10	19:1	109.8	1.10	90031	0.0989	100C
11	27:3	151.79	1.26	4494	0.0068	200C
12	28:2	153.65	1.28	5477	0.0084	200C
13	19:1	119.33	1.19	66369	0.0792	150C
14	19:1	125.78	1.26	2532	0.0032	225 C

Table 3 Resistivity and growth rate of ITO samples with different In : Sn cycle

We also investigated the deposition temperature impacts on the resistivity, and found that higher deposition temperature can lower the ITO resistivity (Figure 11). By increasing the ALD deposition temperature from 200℃ to 225℃, the ITO resistivity drops from $7.4\times 10^{-3}\Omega\cdot$cm to $3\times 10^{-3}\Omega\cdot$cm. 225℃ is the highest deposition temperature we could find from the existing literatures about TMIn precursor, and higher deposition temperature has the risk of TMIn decomposition, so we didn't try higher deposition temperatures.

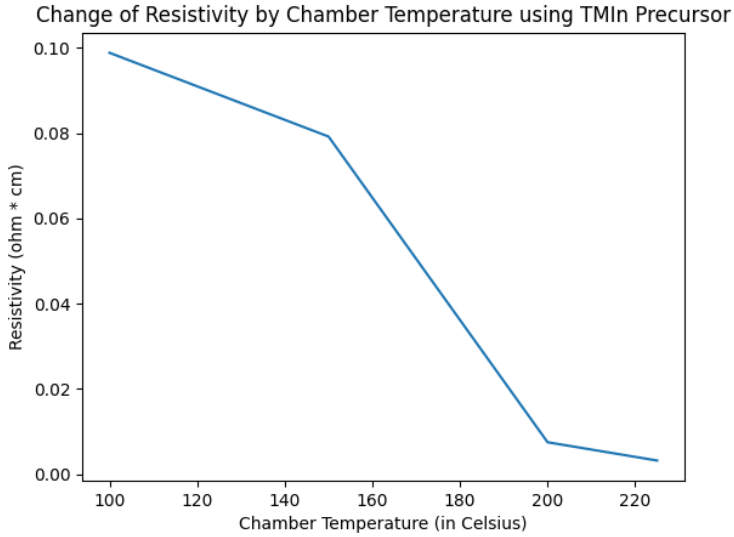

Figure 11 Resistivity of ITO by changing ALD deposition temperature

The lower resistivity at higher ALD deposition temperature indicates that high temperature annealing after deposition may be a better way to achieve low resistivity. However, the annealing conditions for different literatures [4-7] vary a

lot: annealing temperature ranging from 220℃ to 450℃, annealing time ranging from 60s to 4hr, and annealing gas from O_2 to air. It will difficult and time-consuming to find the optimal annealing conditions. We tried annealing at 300℃ for 120s in Ar using the aw_610r RTA tool in SNF on two samples and found the resistivity was successfully lowered. For Fiji4 InCp ITO, the resistivity changed from $4\times10^{-3}\,\Omega$·cm to $1.7\times10^{-3}\,\Omega$·cm. For Fiji4 TMIn ITO, the resistivity changed from $3\times10^{-2}\Omega$·cm to $4.6\times10^{-3}\Omega$·cm. Nathalie will keep working on this to optimize the annealing conditions.

6. Summary and future plan

In this E241 project, we developed ALD In_2O_3 and ITO recipes with InCp precursor by Fiji2 and TMIn precursor by Fiji4. An optimized In_2O_3 recipe has been created for each Fiji tool by finding the saturation curves with respect to In precursor pulse time and the plasma pulse time. After that, a series of ALD ITO films were fabricated using the optimized In_2O_3 recipe and a well-developed SnO_2 recipe at different cycle ratios. The film characterization included the thickness, resistivity, and atomic concentration through XPS. We investigated the relationship between In:Sn cycle ratio and ITO resistivity and measured the XPS atomic concentration of In for each ITO sample. Compared to Fiji4 ITO using TMIn precursor, the resistivity of ITO with InCp precursor by Fiji2 was five times lower but the growth rate per cycle was less stable. The less stable GPC is probably because Fiji2 is a shared tool in SNF for depositions with different materials, and the chamber environment varies during each deposition. On the contrary, Fiji4 is a lab tool owned by prof. H.-S. Philip Wong's group and only has been used for this project in recent years, hence we believed that it can keep the chamber condition more stable.

The resistivity of Fiji4 ITO can be further improved in the future. Several possible reasons can cause high film resistance. One of the possibilities is a deviation between the actual substrate temperature inside the chamber and the temperature we set on the screen. The high carbon concentration detected by XPS would also introduce more crystal defects in ITO film, resulting in less conductive film. Additionally, postdeposition annealing may help to decrease film resistivity. [6] reported a decrease of TMIn In_2O_3 resistivity after postdeposition annealing at 400°C in 500sccm O_2 for 4hrs. The crystallization during high-temperature annealing can lead to lower resistivity.

Reference:

[1] Mane, Anil U., et al. The Journal of Physical Chemistry C 120.18 (2016): 9874-9883.

[2] Elam, Jeffrey W., et al. The Journal of Physical Chemistry C 112.6 (2008): 1938-1945.

[3]https://snfexfab.stanford.edu/docs/presentation/physical-and-electrical-

characterization-of-sputtered-ito-films-for-use-as-solar-cell-electrodes-as
[4] D.-J. Lee, J.-Y. Kwon, J. I. Lee, and K.-B. Kim, J. Phys. Chem. C 115, 15384 (2011).
[5] C. Brahim, F. Chauveau, A. Ringuedé, M. Cassir, M. Putkonen, and L. Niinistö, J. Mater. Chem. 19, 760 (2009).
[6] 40A. U. Mane, A. J. Allen, R. K. Kanjolia, and J. W. Elam, J. Phys. Chem. C 120, 9874 (2016).
[7] Mahmoodinezhad, Ali, et al. "Low-temperature atomic layer deposition of indium oxide thin films using trimethylindium and oxygen plasma." Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 39.6 (2021): 062406.
[8] Elam, Jeffrey W., et al. "Atomic layer deposition of indium tin oxide thin films using nonhalogenated precursors." The Journal of Physical Chemistry C 112.6 (2008): 1938-1945.
[9] Zhao, Bo, et al. "Atomic layer deposition of indium-tin-oxide as multifunctional coatings on V2O5 thin-film model electrode for lithium-ion batteries." Advanced Materials Interfaces 7.23 (2020): 2001022.