Atomic Layer Deposition of Zinc Oxide

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Introduction

Zinc oxide (ZnO) is a promising material for use in microelectronics and photovoltaics applications. It is a wide bandgap semiconductor and can be doped with oxygen vacancies or dopants such as aluminum, making it useful as a transparent conducting oxide layer for organic photovoltaics [1]. Recent work has shown that ZnO can also be a potential candidate for use in metal-insulator-semiconductor (MIS) contacts due to its low conduction band offset to silicon and other common semiconductors [2]. MIS contacts can be used in a variety of applications, ranging from low resistance source-drain contacts to selective contacts for solar cells [3].

The attractiveness of ZnO is increased by its simplicity and the ease by which it can be synthesized in thin-film form using a variety of techniques, including atomic layer deposition (ALD). ALD is a chemical deposition method based on self-limiting, saturated surface reactions that result in highly conformal films and afford a great deal of control over the growth of the film. During ALD coating, two or more chemical vapors or gaseous precursors react sequentially on the substrate surface, producing a solid thin film.

The Zn precursor used in the Savannah ALD system in SNF is diethyl zinc (DEZ) which reacts readily with H_2O through the following mechanism [4]:

$$Zn(C_2H_5)_2^* + H_2O(g) \rightarrow ZnO^* + 2C_2H_6(g)$$

It has been shown that different ALD growth parameters have a large impact on properties of the film [5]. The goal of this project is to characterize the material quality and electrical properties of zinc oxide deposited using various growth conditions in the Savannah ALD chamber in SNF. In particular the influence of deposition temperature on ZnO properties will be explored in detail.The properties of interest include film stoichiometry, resistivity, and carrier concentration.

Methodology

The process flow for the deposition of zinc oxide consisted of 4 steps: RCA clean, thermal oxidation, RCA clean, and ALD of ZnO. The initial RCA clean was done on bare Si wafers prior to the oxidation step. The bare silicon wafers used were then thermally oxidized in Thermco2 before the ZnO ALD. A wet oxidation was done for 45 minutes at 1000°C to grow approximately 300 nm of SiO_2 on top of which the ZnO would be deposited. The purpose of the SiO_2 layer was to insulate the ZnO film from the silicon substrate. Since the zinc oxide was expected to be conductive, this insulating layer prevents the leakage of current into the Si

substrate which would give erroneous results when doing electrical characterization of the ALD films.

Immediately prior to the ALD step the oxidized wafers underwent another RCA clean to ensure that the surface was free of any contamination. After this clean, the SiO_2 thickness was measured on each wafer using a 9 point scan on the Woollam M2000 Spectroscopic Ellipsometer. All of the samples showed very uniform SiO_2 thickness with less than 1 nm variation across the wafer.

ALD Zinc Oxide Recipe Development

DEZ pulse time

Before studying the effects of deposition temperature on ZnO film properties, the effect of the DEZ precursor pulse time was investigated. The DEZ pulse times were varied from 0.03s to 0.3s, and the effects on the ZnO thickness and uniformity were measured. The other variables on the Savanah tool were kept constant, and the values are summarized in Table 1 below. It was noted that the 20s purge times after each of the precursor pulses was enough to ensure that the chamber returned to its base pressure before the next pulse. In addition, 200 cycles were deposited for each deposition in order to ensure that the resulting ZnO film would be thick enough to measure using ellipsometry.

Parameter	Value
Nitrogen carrier gas flow	20 sccm
DEZ temperature	unheated
DEZ purge time	20s
H_2O pulse time	0.015s
H_2O purge time	20s
Number of cycles	200

Table 1. Control parameters for ZnO ALD

The first run was done with the DEZ pulse time set to 0.3s. The resulting pressure spikes, shown in Figure 1, were measured to range from 1.3-1.4 torr, which was nearly four times higher than the water vapor pulses. This indicates the DEZ was overdosed, which results in a process more similar to standard CVD with high non-uniformity in the chamber.

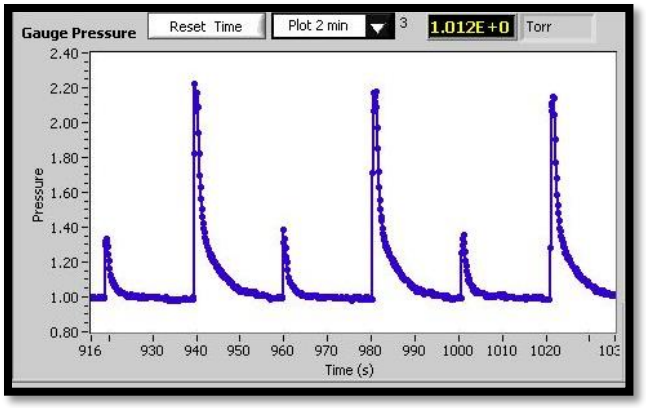
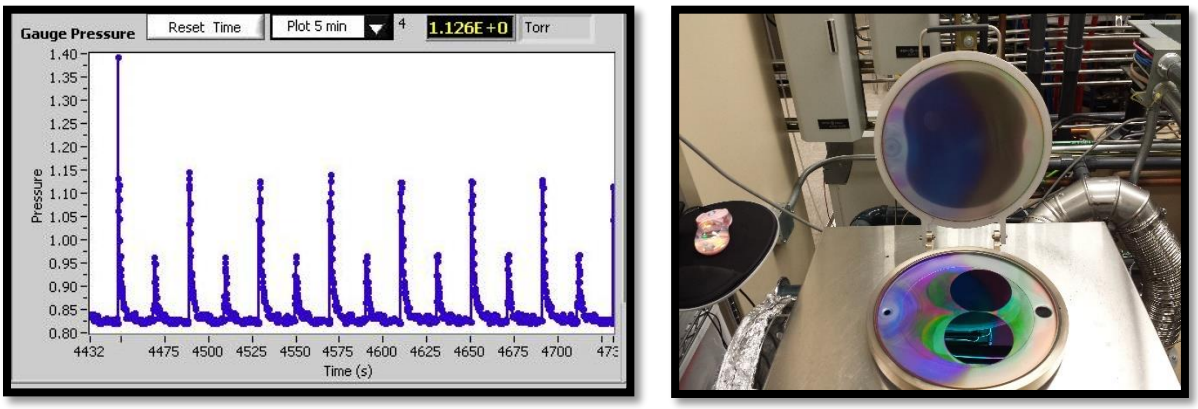


Figure 1. Overdosing with 0.3s DEZ pulse time

For the second run the DEZ pulse time was 0.03s with a corresponding pulse height of 0.1-0.15 torr as seen in Figure 2a. In this case the precursor was underdosed, meaning there was not enough DEZ to fully cover the chamber. Figure 2b shows that there was only enough DEZ to cover about half of the chamber and thus there was only ZnO deposition on the half closer to the gas inflow.



(a) (b)

Figure 2. Underdosing with 0.03s DEZ pulse time

For the third run the DEZ pulse time was set to 0.06s, resulting in a pulse height of 0.15-0.2 torr. This ensures there is enough of the precursor to fully coat the chamber but not so much that it cannot be fully purged from the chamber before the next pulse.

In order to study the deposition temperature effect on ZnO film properties, 7 different deposition temperatures were tested in Savannah. The third run we set the DEZ pulse to 0.06s and the DEZ pulse height was 0.2 torr, shown in Figure 3. This gives much better deposition uniformity compare to former runs. Proper dosing ensures that the deposition process is self-limiting, which results in uniform and high quality films. Table 2 summarizes the effect of DEZ pulse time on ZnO deposition.

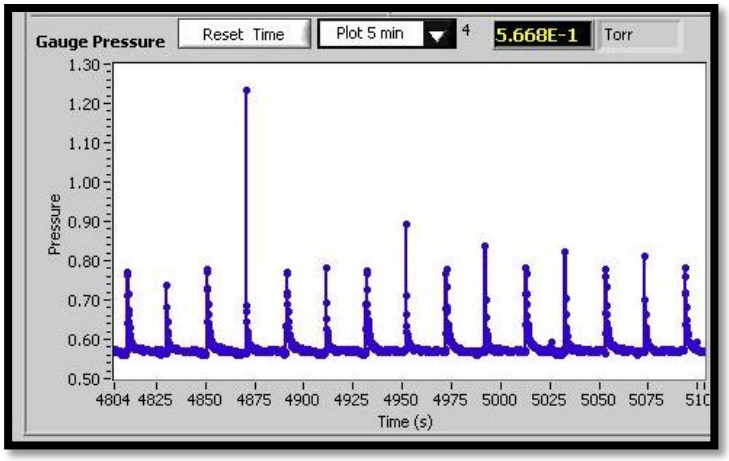


Figure 3. Proper dosing with 0.06s DEZ pulse time

DEZ pulse time	DEZ pulse height	Comments
0.03s	0.1-0.15 torr	Underdosing
0.06s	0.2 torr	Proper dosing
0.3s	1.3-1.4 torr	Overdosing

Table 2. Effect of DEZ pulse time on ZnO ALD

Deposition Temperature

The main focus of this project was to determine the effects of deposition temperature on ZnO grown using ALD. In particular, the growth rate, uniformity, film stoichiometry, carrier concentration, and electrical resistivity were investigated. All of the depositions were done with a DEZ pulse time of 0.06s to ensure good uniformity as it was seen that the pulse height did not change significantly with deposition temperature. Studies have shown that the nominal ALD window for ZnO on Si ranges from 130-170°C [4]. In this study, the chamber temperature was varied from 100°C to 250°C in 25°C intervals, resulting in a total of seven different deposition temperatures. The results from these depositions are presented below.

Deposition Rate and Uniformity

The chamber setup in Savannah for the seven ZnO depositions is shown in Figure 4. Two 4-inch wafers are placed adjacent to each other in the direction of the carrier gas flow with the major flat facing toward to front. Two dummy half-wafer pieces are placed at the front and back of the chamber to minimize movement of the samples during the deposition. At the end of each run, nitrogen is run through the chamber at 20 sccm for 10 minutes to ensure that any metallic zinc is

removed from the chamber. Once the wafers are removed, 100 cycles of the standard HfO_2 recipe are deposited in the empty chamber to encapsulate any remaining particles and prevent contamination issues for other users.

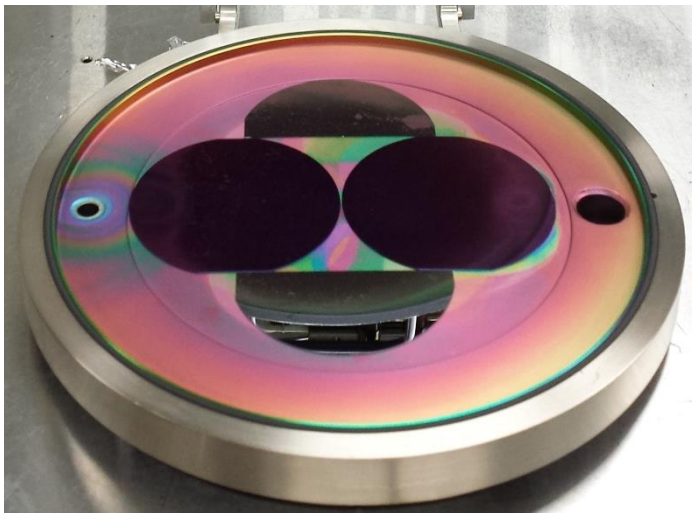


Figure 4. Wafer setup in Savannah chamber

In order to measure the thickness of the deposited ZnO films, the Woollam M2000 was used. A 9-point scan was done on each of the wafers to determine the uniformity across the chamber. Due the similar optical properties of SiO_2 and ZnO, it was found that the ellipsometer could not accurately determine the boundary between both materials. In order to combat this issue, the SiO_2 thickness was measured before each ALD run, and this value was used when fitting the ZnO thickness on the Woollam.

The thickness statistics for each of the 7 runs are summarized in Table 3, and the average growth rate versus temperature is graphed in Figure 5. The average growth rate slightly increases going from 100°C to 125°C but otherwise steadily decreases going to higher temperature as is expected with ALD reactions. The most important takeaway from the thickness measurements is the significant increase in standard deviation for depositions done at 200°C and higher. For all of the depositions done below 200°C the total variation in the chamber was less than 1 nm, indicating highly uniform ALD, but at higher temperature the variation in the chamber was upwards of 3nm. This suggests we are outside of the ALD window, resulting in very nonuniform and low-quality zinc oxide films. Figure 6 shows a thickness mapping of the deposited ZnO throughout the chamber for each deposition temperature

Temperature	Min (Å)	Max (Å)	Average (Å)	Standard Deviation (Å)	Deposition Rate (Å/cycle)
100°C	377.82	391.18	384.93	3.66	1.92
125°C	396.48	413.09	407.88	4.12	2.04
150°C	297.20	305.54	301.48	2.02	1.51
175°C	289.17	295.48	292.81	2.00	1.46
200°C	218.27	278.62	246.18	18.56	1.22
225°C	184.12	222.91	204.06	17.13	1.02
250°C	53.96	116.35	74.57	18.11	0.37

Table 3. Thickness and uniformity statistics as a function of deposition temperature

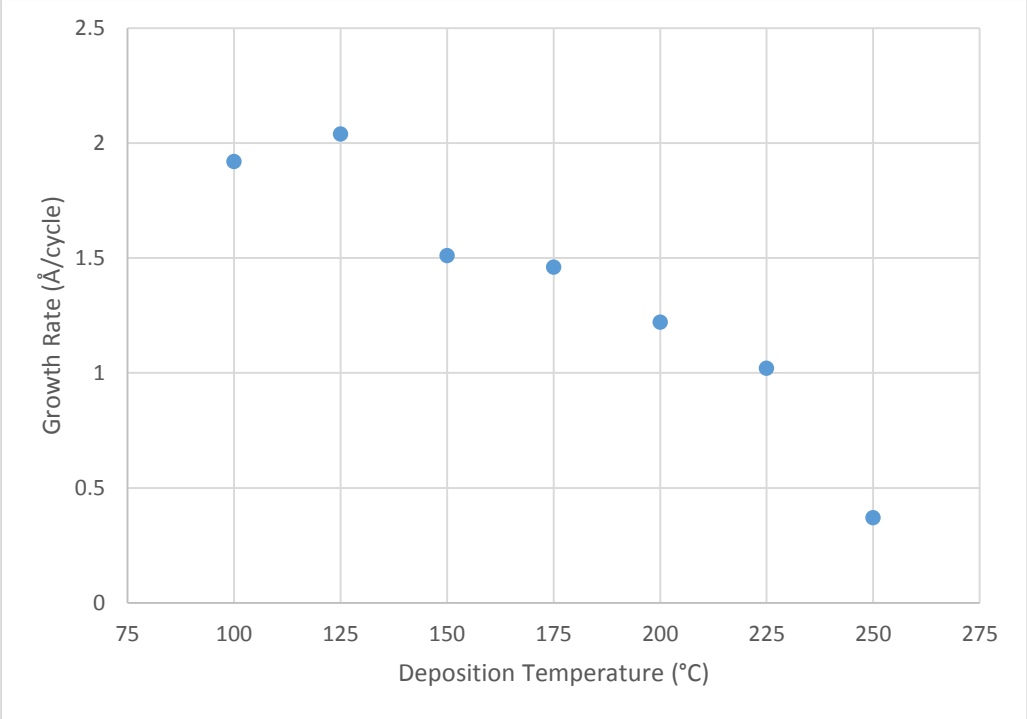


Figure 5. ZnO growth rate as a function of deposition temperature

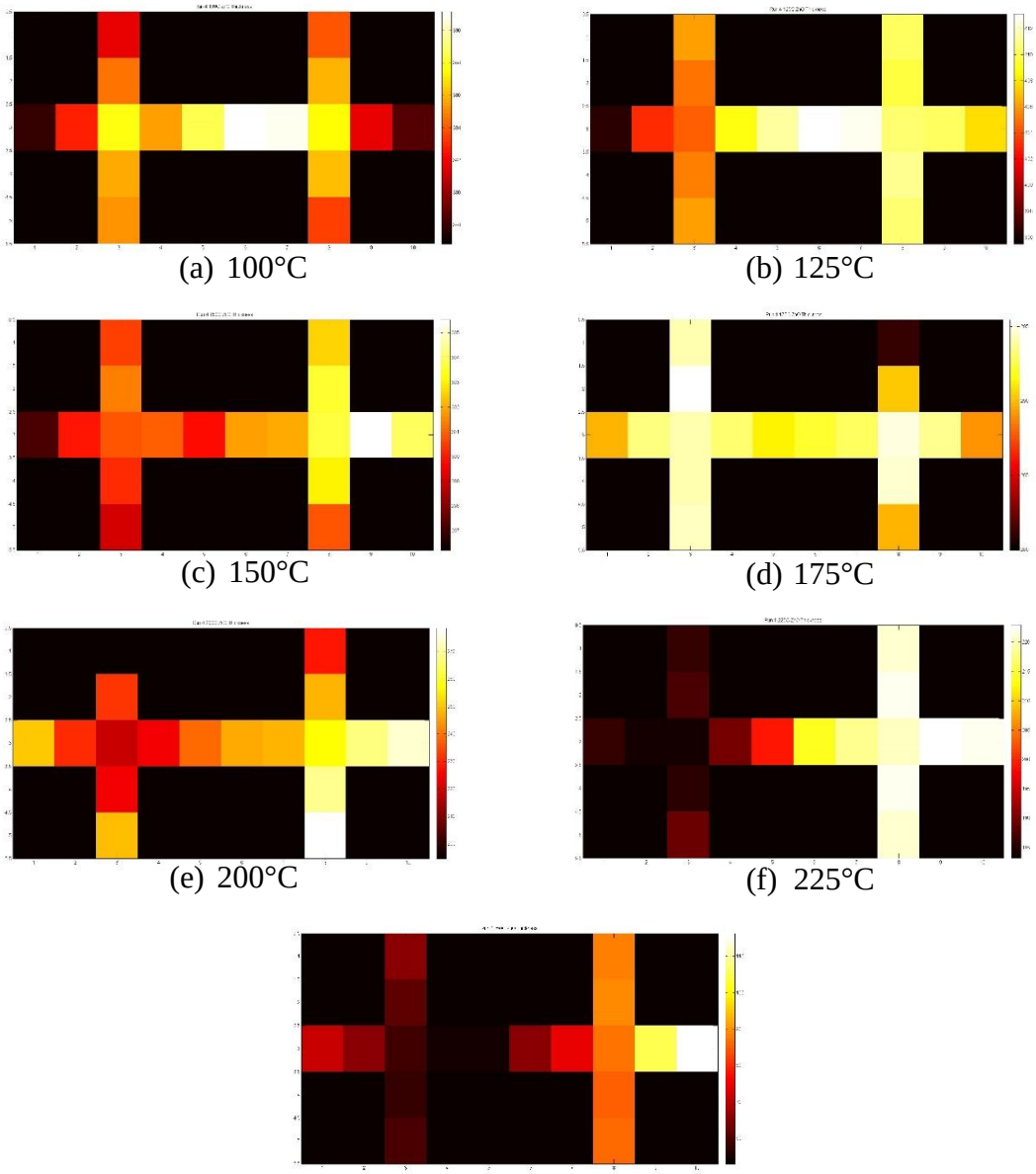


Figure 6. Thickness mappings throughout the chamber for ZnO depositions

Stoichiometry of ALD Zinc Oxide

The composition of the ZnO films were measured using the PHI XPS tool in SNL. A 20 μm x-ray beam spot size was used to ensure that the data was representative of a large area of the film. The neutralizer was also turned on during the measurements in order to compensate for charging effects since the zinc oxide layer is insulated from the silicon substrate by a 300 nm layer of SiO_2.

A survey scan was initially performed on each sample to ensure that there was not significant contamination from other elements present on the surface (Figure 7). High resolution scans were then performed on the Zn 2p3, O 1s, and C1s peaks. A high resolution peak of the Zn 2p3 peak is

shown in Figure 8a. Both metallic zinc and ZnO have peaks centered at 1021.6 eV so only one peak was visible for all of the samples measured. The O 1s peak (Figure 8b) was seen to be separated into two distinct peaks, corresponding to Zn-O (lower binding energy) and C-O (higher binding energy) bonding. A Gaussian peak fitting procedure was done to determine the relative percentage of oxygen in each bonding state.

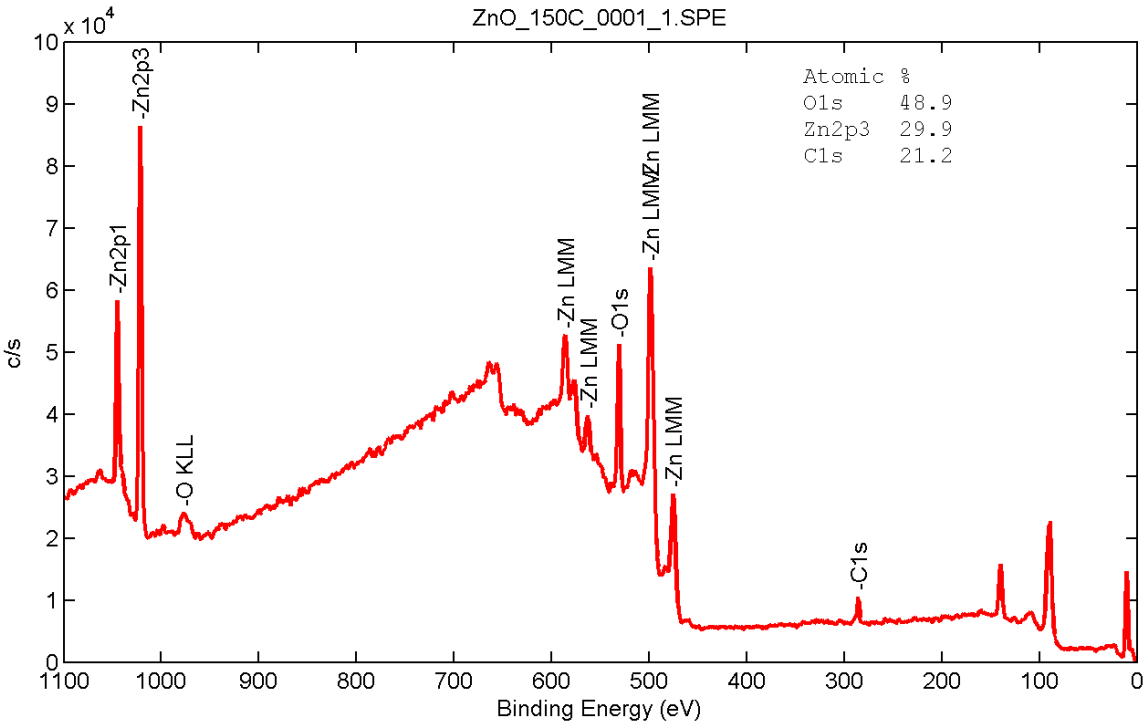
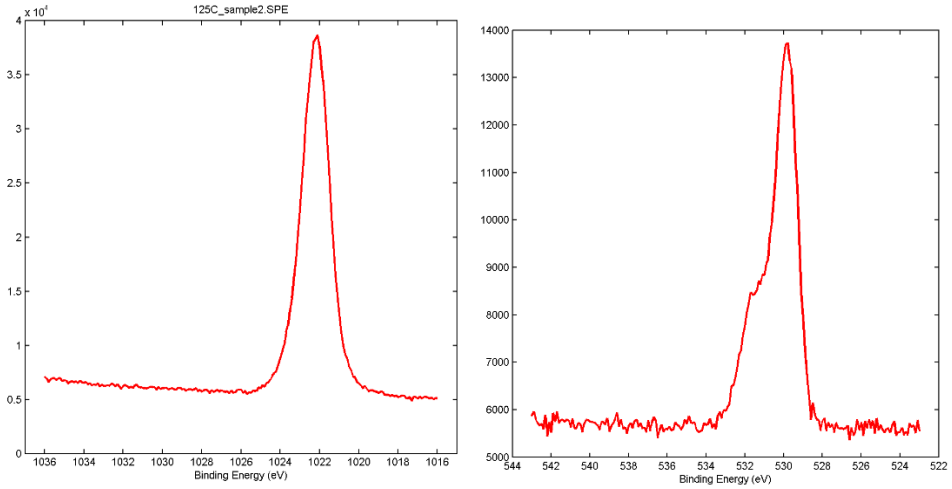


Figure 7. Survey scan of XPS measurements on ALD ZnO



(a) Zn 2p3 peak (b) O 1s peak

Figure 8. High resolution XPS scans

The extracted O:Zn ratios for the seven ALD ZnO samples are summarized in Figure 9. The film stoichiometry is nearly constant in the range of 125°C to 200°C, with O:Zn being approximately 0.7. This data suggests stable and controlled growth within this temperature window. However, the ALD films are highly oxygen deficient, indicating the dosage of H_2O during the deposition was not enough to achieve stoichiometric ZnO. Increasing the pulse time or the number of pulses between ZnO pulses may help to increase the oxygen content.

Outside of this temperature range (100°C, 225°C, 250°C) the oxygen content begins to increase dramatically, with measurements suggesting deposition at 250°C yields oxygen rich zinc oxide. However, it was noted that XPS measurements done at various locations on these wafers yielded variable O:Zn ratios. It is therefore speculated that outside of the ALD window the deposition is nonuniform not only in thickness but also film stoichiometry itself.

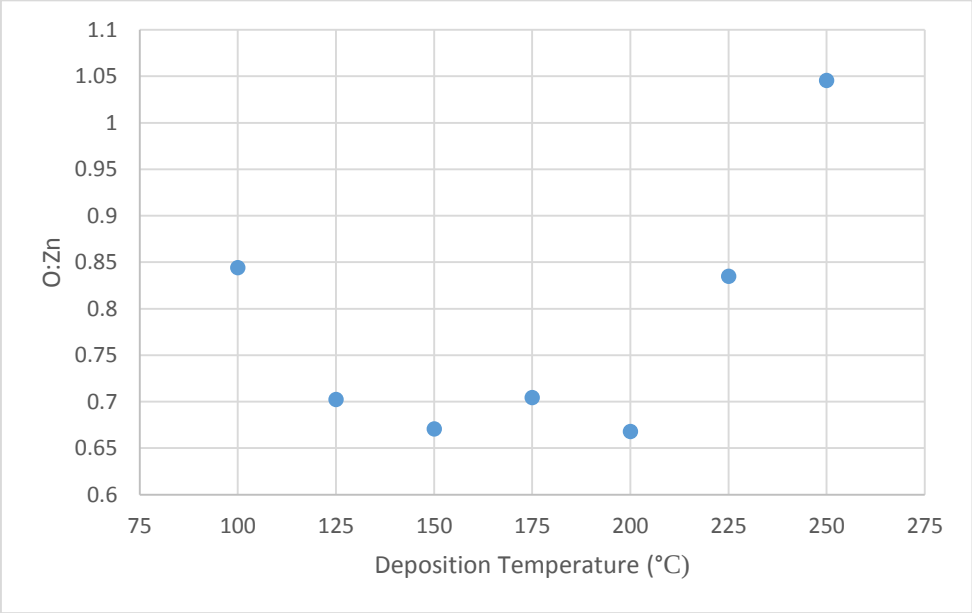


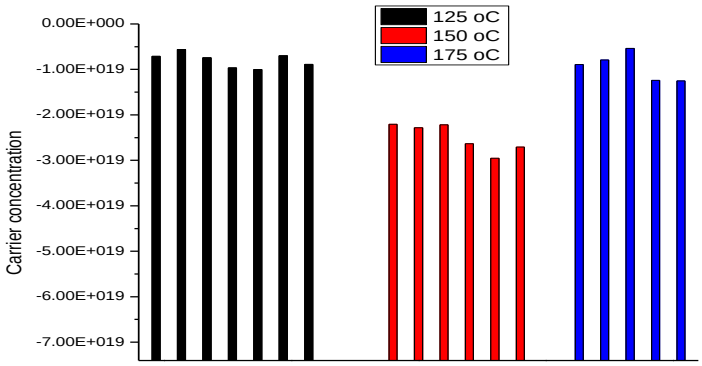
Figure 9. Variation of film stoichiometry with deposition temperature

Electrical Characterization

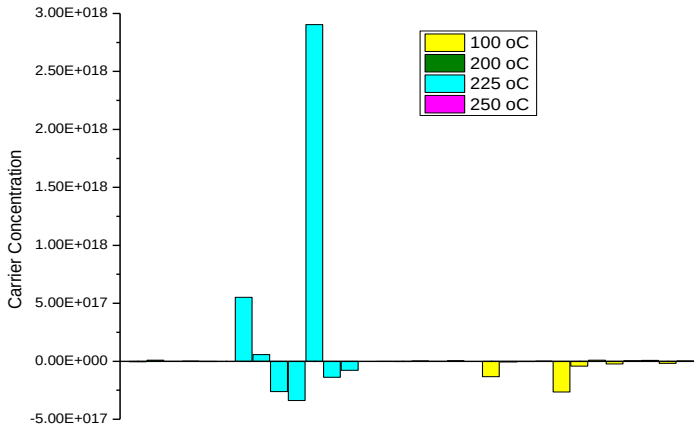
Hall measurements were done on the ALD ZnO films to determine the electrical conductivity and carrier concentrations for depositions at different temperatures. The samples were prepared by cleaving the wafers into 1cm x 1cm pieces. Indium contacts were then manually pressed onto the 4 corners of the pieces. It was found during the measurements that contact preparation is critical in getting accurate and repeatable measurements. If a good ohmic contact is not made, the contact resistance dominates and it is difficult to extract the resistivity of the ZnO film itself. Since the contacts were placed manually, an IV sweep was done prior to each Hall measurement to ensure good ohmic contact. A linear IV curve indicates proper contacting. Multiple samples were measured from each deposition and each sample was measured multiple times to ensure reliability. Each measurement was done sourcing the highest amount of current possible to ensure good signal-to-noise ratio without overloading the maximum voltage of 10V on the tool.

Figure 10a indicates the carrier concentration extracted from all of the measurements done at 125°C, 150°C, and 175°C. The graph shows that the carrier concentration measurement is consistent and repeatable for each deposition temperature. It should be noted that all of the values are negative, indication n-type ZnO films.

Conversely, the carrier concentration measurements for the depositions at 100°C, 200°C, 225°C, and 250°C are seen in Figure 10b. First, the data showed high variably between measurements. On all of these samples consecutive measurements would sometimes indicated n-type films and sometimes p-type films. This erroneous data made it impossible to determine the exact carrier concentration and resistivity of the ZnO layer. In addition, the absolute value of the carrier concentration was up to four orders of magnitude lower than for the reliable samples. One possible problem may be that the samples are too resistive to make accurate measurements. 1 mA of current was sourced for the good samples deposited at 125°C, 150°C, and 175°C, but the current level had to be lowered to less than 1 µA for the bad samples grown at 100°C, 200°C, 225°C, and 250°C. This current may be low enough that the discrepancies in the carrier concentration could be due to electrical noise.



(a)



(b)

Figure 10. Carrier concentration extracted from Hall measurement

The extracted average carrier concentration and resistivity are summarized in Table 4. The average values are omitted for the samples with unreliable measurements. The carrier concentrations for the depositions at 125°C, 150°C, and 175°C were close to 10^{19} cm^{-3} with the resistivity on the order of 10^{-2} Ω·cm. It is noted that the 150°C deposition shows the highest carrier concentration and highest conductivity.

Temperature	**Carrier Concentration (cm^{-3})**	**Resistivity (Ω·cm)**
100°C	Inconsistent	Inconsistent
125°C	-7.95E+18	2.22E-02
150°C	-2.50E+19	1.34E-02
175°C	-9.71E+18	7.74E-02
200°C	Inconsistent	Inconsistent
225°C	Inconsistent	Inconsistent
250°C	Inconsistent	Inconsistent

Table 4. ZnO carrier concentration and resistivity

Contamination Study of Zinc Oxide Anneal

While the deposition temperature effects were being analyzed, a study was done regarding the high temperature processing of ZnO grown in the Savannah ALD chamber. The following is adapted from the PROM request that was submitted and approved. All of the anneals outlined in the procedure have been completed, and the wafers will be sent out for testing.

Motivation

Metallic zinc is a dangerous contaminant due to its low vapor pressure, and studies have shown that ZnO deposited using ALD typically can have an appreciable amount of metallic zinc. In addition, there was a previous problem in SNF with zinc contamination when ALD ZnO samples grown in the McIntyre lab were annealed in FGA2. Measuring the extent of zinc contamination after high temperature anneals can help determine if ZnO deposited in Savannah could be safe to use on other tools in SNF.

Process Flow

Wafers with ZnO deposited in Savannah were used for this study. Tylan4 was used for the annealing because the tool was removed from the lab, preventing any contamination issues for other labmembers. During each run 3 Si test wafers were placed at different locations in the tube to account for any temperature variations (Figure 11). One wafer was placed in the very center and the other two were placed one boat-length away on either side, as shown in the figure below. The wafers were oriented so that the flat is facing up and the polished side is facing out.

Figure 11. Wafer distribution in Tylan4 for anneal contamination study

Eight different runs were done. Each anneal was done in an N_2 ambient with a dwell time of 20 minutes. The overall process was performed in the order outlined below:

1. Temp: 500°C. Only the test wafers were placed in the tube to have a reference level for zinc contamination.
2. Temp: 700°C. Only the test wafers were placed in the tube to have a reference level for zinc contamination.
3. Temp: 500°C. Wafers coated with zinc oxide were placed in the slots immediately adjacent to the test wafers with the film facing the polished side. This allows us to test for the maximum amount of zinc that will come off the film during the annealing process.
4. Temp: 700°C. Wafers coated with zinc oxide were placed in the slots immediately adjacent to the test wafers with the film facing the polished side. This allows us to test for the maximum amount of zinc that will come off the film during the annealing process.
5. Temp: 500°C. Only the test wafers were placed in the tube to check for any residual zinc in the furnace.
6. Temp: 700°C. Only the test wafers were placed in the tube to check for any residual zinc in the furnace.
7. A Trans-LC clean was done in an attempt to remove any metallic zinc.
8. Temp: 500°C. Only the test wafers were placed in the tube to test the effectiveness of the Trans-LC clean.
9. Temp: 700°C. Only the test wafers were be placed in the tube to test the effectiveness of the Trans-LC clean.

Contamination Test

The test wafers will be sent out in order for the zinc content to be analyzed using ICP-MS. Initially 4 of the test wafers will be analyzed in the following order. Only the middle wafer from each set will be analyzed. The wafers annealed at higher temperature are tested first to give a worst-case estimate of zinc contamination.

1. 700°C before zinc oxide introduced (Step 2)
2. 700°C annealed with zinc oxide (Step 4)
3. 700°C after zinc oxide anneal (Step 6)
4. 700°C after Trans-LC clean (Step 9)

If there is still significant zinc contamination in the furnace even after the Trans-LC clean, the wafers annealed at lower temperature will be tested for contamination in the following order. Only the middle wafer from each set will be analyzed.

1. 500°C before zinc oxide introduced (Step 1)
2. 500°C annealed with zinc oxide (Step 3)
3. 500°C after zinc oxide anneal (Step 5)
4. 500°C after Trans-LC clean (Step 8)

Discussion and Conclusion

A complete summary of all of the experimental results is given in Table 5. The spaces in the table have been color coded, with green qualitatively indicating a good result and red indicating a poor or inconsistent result. The thickness and uniformity measurements showed that depositions below 200°C gave conformal films with less than one 1 nm variation across the chamber, indicating high quality ALD. The depositions done at 200°C and above showed a much lower growth rate and a large thickness deviations, similar to what is seen in a CVD process. This data is similar to reports in literature that the ALD window for ZnO ranges from 130-170°C.

It was expected that the XPS measurements would show ZnO films with well-defined stoichiometry for the depositions that had good uniformity. This was the case outside of the deposition done at 100°C. However, the deposition done at 200°C showed O:Zn ratio of nearly 0.7, similar to that of the runs completed from 125°C to 175°C. This slight discrepancy can be attributed to the fact that 100°C and 200°C are slightly outside of the nominal ALD window but are still close enough in temperature that the film quality is not significantly altered.

One interesting outcome from the experiments is that nearly all of the depositions resulted in highly oxygen deficient films. While ALD ZnO is expected to be oxygen deficient, the O:Zn ratio is typically reported to be close to 0.9 as opposed to 0.7 [4]. Since the XPS has a depth profile of approximately 5nm, it is postulated that low oxygen content is due to weak bonding between O and Zn at the surface or long exposure to air between the time of deposition and XPS measurement. In the future argon sputtering will be used to generate the atomic composition depth profile and better understand the large deficiency in oxygen.

As previously reported the Hall measurements were inconsistent and unreliable for the ZnO grown at 100°C, 200°C, 225°C, and 250°C. Once again, these temperatures are expected to be outside of the ALD window. The Hall measurement tool assumes the underlying film is highly uniform, and any nonuniformity in terms of thickness or material composition can result in erroneous results. Work was also done to ensure that ohmic contacts were formed, but the process of manually placing indium on the pieces still introduces sample to sample reliability. For future work metal contacts will be evaporated to ensure better reliability of the contacts.

From the XPS measurements, which showed similar composition for the depositions done at 125°C, 150°C, and 175°C, it would be assumed that the carrier concentration and resistivity would also be similar for the three samples. The 150°C ZnO did give slightly higher concentration and lower resistivity, but this can be explained by the lower oxygen content in the film. Though the general trends are reasonable, such low oxygen content should result in much higher carrier concentrations up to 10^{21} cm^{-3} [4]. The assumption that the films are more oxygen deficient near the surface may explain the discrepancy between material composition and electrical measurements. The film stoichiometry depth profile measurement using argon sputtering can help better explain these results.

In conclusion, a standard ZnO recipe was developed in the Savannah ALD tool in SNF. A deposition temperature study was done, and the uniformity, film stoichiometry, carrier concentration, and resistivity were all measured. The results indicate that the ALD window on this tool ranges from 125°C to 175°C. Depositions done in this range yield highly uniform films with good electrical conductivity. Further work is ongoing to further characterize the film composition and to grow ZnO thin films with lower resistivity.

Temperature	**Deposition Rate (Å/cycle)**	**Standard Deviation (Å)**	**O:Zn ratio**	**Carrier Concentration (cm^{-3})**	**Resistivity (Ω·cm)**
100°C	1.92	3.66	0.84	Inconsistent	Inconsistent
125°C	2.04	4.12	0.70	-7.95E+18	2.22E-02
150°C	1.51	2.02	0.67	-2.50E+19	1.34E-02
175°C	1.46	2.00	0.70	-9.71E+18	7.74E-02
200°C	1.22	18.56	0.67	Inconsistent	Inconsistent
225°C	1.02	17.13	0.83	Inconsistent	Inconsistent
250°C	0.37	18.11	1.05	Inconsistent	Inconsistent

Table 5. Summary of experimental results

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