Atomic Layer Deposition of Aluminum Doped Zinc Oxide

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Abstract

The major attraction for aluminum doped zinc oxide (AZO) is due to its large band-gap and large excitation energy, which is an excellent candidate for various applications such as optoelectronics, photoelectric, and transparent electronic devices. However, producing a uniform AZO film and composition with a desirable electronic property is still a challenge. Here, we demonstrate that AZO could be successfully deposited by atomic layer deposition Technique(ALD). The results show that the thickness of AZO deposition is uniform (<1.8 nm variation across the entire wafer), and all of AZO films deposited by ALD show promising electrical properties.

1. Introduction

Aluminum doped zinc oxide (AZO) has been extensively studied in various applications such as optoelectronic, photoelectric, and transparent electronic devices. Aluminum is one of the widely used dopants in zinc oxide (ZnO) to control the electrical properties such as mobility and resistivity. [1, 2] Recent studies have shown that AZO is one of the promising materials for ITO replacement not only its low resistivity value on the order of $10^{-4}\Omega$cm [3] comparable to that of ITO but also its low cost, earth abundance, and non-toxic property. [4, 5] A numerous researches have been reported that AZO can be grown by sputtering, [6] chemical vapor deposition, [7] and so-gel methods. [8] However, how to precisely control film composition and electronic properties are important especially for nanoscale applications, and aforementioned techniques are hard to tune the thin film properties and conformal film deposition at the nano-scale. In addition, with the newly explored organic and flexible electronics, a deposition technique with low deposition temperature is required. [9] Those requirements could be met with atomic layer deposition (ALD). ALD is a kind of chemical vapor deposition, and it can not only control the film growth within a sub-nanometer precision but also operate at a relative low temperature window (below 200 °C). [9,10] Therefore, in order to achieve high quality AZO film, ALD is one of the best deposition techniques to investigate. In this study, we have successfully demonstrated that we can deposit AZO with good uniformity and predictable electrical performances by using ALD. The quality of AZO growth by ALD technique is excellent, and thickness of film along with the entire deposited area could be controlled with a less than 1.8 nm thickness error. In addition, dopant concentration and electrical properties of AZO are further studied and reported.

2. Methodology

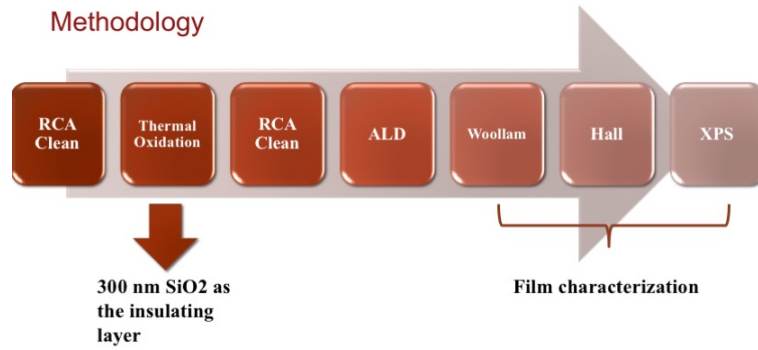The general process of AZO film along with the characterization is described in the Fig.1.

Fig. 1: Overall methodology and process flow

Prior to each ALD deposition, fresh wafers were cleaned through the standard RCA cleaning protocol to remove any organic, metal and oxide contaminants, followed by 300 nm thermally grown SiO_2 to create a buffer layer for electrical analysis. Then, Si/SiO_2 wafers were processed again with RCA cleaning for the AZO growth.

1. ALD of AZO

AZO was grown by ALD equipment (Savannah S200, Cambridge Nanotech), which is capable to accommodate up to 8-inch wafer. For each growth, two full-size wafers, one placed at the top and another one at the bottom, were deposited simultaneously.   Diethylzinc (DEZ, $Zn(C_2H_5)_2$), water (H_2O), and Trimethylaluminum (TMA, $Al(CH_3)_3$) were used as the basic precursors to grow AZO. During ALD deposition, the chamber temperature was controlled at 150 ^{0}C while the precursor delivery line was maintained at 140 ^{0}C. And the nitrogen was used as a carrier and purging gas with a flow rate of 20 sccm. Table 1 summarized the general process flow of ALD of AZO film, which was developed by adapting the previous EE 412 ZnO project and R. M. Mundle et al's study. [11, 12] Two iterative cycles were presented. The first cycle, which refers as X-micro cycle, controlled the Zn to Al deposition ratio. The second cycle, which refers as Y-macro cycle, controlled the film thickness. First, based on the flow chart, as shown in Table 1, ZnO was deposited on the film until X number of cycles reached. Then, TMA, $Al(CH_3)_3$ was introduced by one cycle, followed by the repetition of X-micro cycle. The total process will continue to repeat between X and Y macro cycles until number reached to the number of Y. Afterward, the growth process was completed, which was ready for thickness and electrical characterizations. The amount of Al deposition was controlled by manipulating the numbers of X and Y.

Process #	Instruction	Value
0	N_2 Flow [sccm]	20
1	Inner heater T [C]	150
2	Outer heater T [C]	150
3	Precursor manifold heater T [C]	140
4	Stop valve heater T [C]	150
5	Stabilize precursor manifold heater	

6	Stabilize outer heater	
7	Stabilize inner heater	
8	Wait [s]	300
9	Pulse DEZ, $Zn(C_2H_5)_2$ [s]	0.03
10	Wait [s]	40
11	Pulse H_2O [s]	0.015
12	Wait [s]	45
13	Goto Zn Pulse #9	X
14	Pulse TMA, $Al(CH_3)_3$ [s]	0.015
15	Wait [s]	40
16	Goto Zn Pulse #9	Y
17	Wait [s]	300
18	Flow [sccm]	5

Table 1: General process flow of ALD of AZO

3. Results

1. Characterization – thickness and growth rate of ZnO and AZO
After successful deposition of AZO, the thickness of films was further characterized using Woollam M2000 Spectroscopic Ellipsometer. To check the uniformity across the entire wafer, 9-point scan was used. Prior to full AZO film thickness characterization, the thickness of SiO_2 was required to be determined because SiO_2, ZnO, and AZO had similar optical properties, which ellipsometer could not accurately estimate the boundary between those materials. After the thickness of SiO_2 was determined, the final thickness of AZO could be readily obtained by setting SiO_2 thickness as a known information.

The maximum, average, and minimum film thickness and the average growth rate of wafers are plotted in Fig. 2. The average growth rate was calculated by dividing the average film thickness by the number of total cycles. The average film thickness is between 17.4nm and 24.5nm except 40:1 AZO, which shows an abnormal growth. The biggest thickness variation (Max – Min) and standard deviation across the entire project are 1.8nm and 0.5nm, respectively in 20:1 AZO growth. The possible explanation can be that 20:1 AZO growth wafers may have less uniform SiO_2 substrates. The average growth rates show consistent values between 1.37A/cycle and 1.74A/cycle, excluding 40:1 AZO, which will discuss more in detail in appendix section: pressure monitoring study.
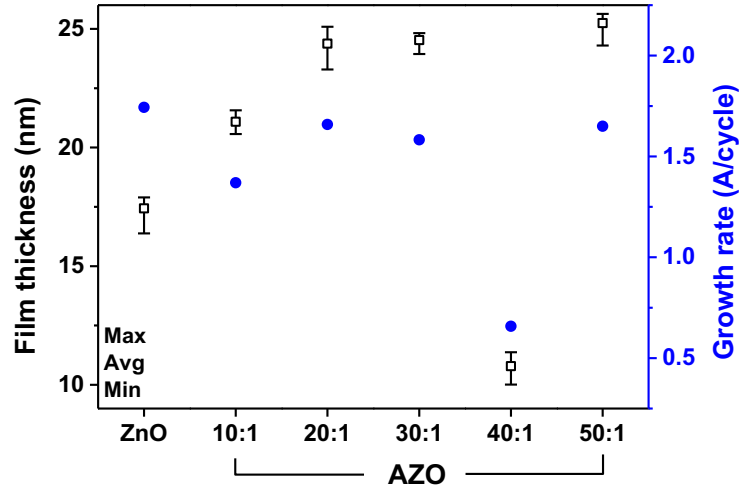
Fig. 2: Film thickness and growth rate of ZnO and AZO

2. Stoichiometry of ALD Aluminum doped Zinc Oxide

After the thickness of AZO is determined, the composition of the ZnO films and Al doped ZnO (AZO) 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 ALD thin layers are insulated from the silicon substrate by a 300 nm layer of SiO_2. Three survey scans were performed on each sample to ensure that there was not significant contamination from other elements present on the surface (Fig. 3). Both ZnO and Al doped ZnO have peaks centered at 1021.6 eV so only one peak was visible for all of the samples measured. Weak Al peaks can be seen from Fig. 4.
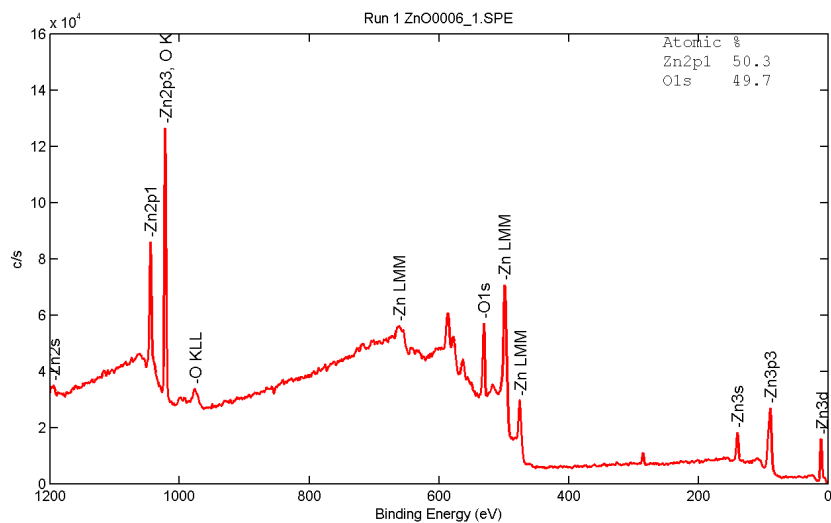
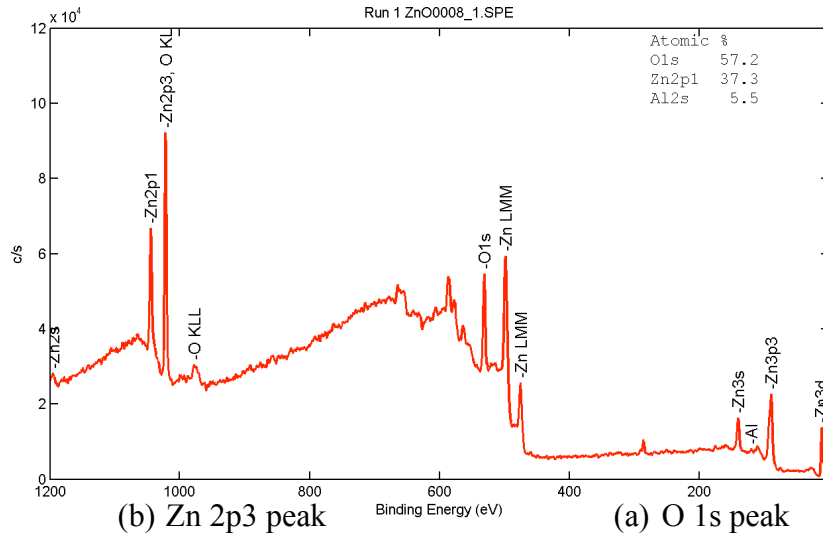

Fig.3: Survey scan of XPS measurements on ALD ZnO

Fig. 4: Survey scan of XPS measurements on ALD AZO with Zn:Al=20:1

The extracted Zn:Al:O ratios for the five ALD Al doped ZnO samples are summarized in Table 2. The film stoichiometry is nearly constant for the intrinsic ZnO, with Zn:O being approximately 1. This data suggests stable and controlled growth within this temperature window. For Al doped ZnO sample, the Al concentration trend matches well with the ALD cycles we designed for the ALD deposition. XPS results shows a decreasing trend in Al concentration from Zn to Al ratio 10:1 to 50:1. For 40:1 samples, however, due to the precursor issues, highly non-uniform films were obtained which wasn't included in the XPS test.

Name	Zn(%)	Al(%)	O(%)
ZnO	50.3	0	49.7
AZO 10:1	29.5	7.6	63
AZO 20:1	37.3	5.5	57.2
AZO 30:1	52.9	4.7	42.4
AZO 50:1	52.2	1.8	46

Table 2: Summary of element concentration for different ALD films

3. Electrical Characterization

Hall measurements were done on the ALD ZnO and Al doped ZnO films to determine the electrical conductivity and carrier concentrations for depositions at different Al concentrations. The samples were prepared by cleaving the wafers into 1cm x 1cm pieces. A shadow mask is used to deposit 50nm thick Au films at four corners serve as the contacts during the measurement. 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. For each measurement, 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. Since all the samples showed good conductivity, each measurement was done with the same high current to ensure a good signal-to-noise ratio and to make a good comparison. For 40:1 Al doped ZnO sample, no Hall measurement results was obtained due to the non-consistent film coverage which caused super high contact resistance.

Figure 5a indicates the carrier concentration extracted from all of the measurements. The graph shows that the 10:1 Al doped ZnO sample has the highest carrier concentration which might due to the high Al doping concentration. 20:1 and 50:1 AZO showed similar bulk concentrations which are slightly higher than the 30:1 AZO and pure ZnO. It seems that at lower level doping concentrations, Al atoms has less influences on the thin film bulk concentrations. The carrier concentration measurement is consistent and repeatable for all conditions. It also should be noted that all the values are negative, indication n-type ZnO and AZO films were deposited for our project. The charge carrier mobility data is shown in Fig. 5b, which shows a converse trend with bulk concentration data. 10:1 AZO samples showed the lowest charge carrier mobility which might due to the high charge carrier concentration within the film. 20:1 and 30:1 AZO films showed highest mobility which corresponding well with the resistivity data in Fig. 5c. It is worth noticed that all samples showed low resistivity within the 10^{-2} range which indicates our recipe works well for repeatable, uniform and conduction thin film deposition.

The extracted average carrier concentration, mobility and resistivity are summarized in table 3. The carrier concentrations for the depositions at different conditions within the range of 10^{19} cm^{-3} except the 10:1 AZO showed 10^{20} cm^{-3}. Overall, all the films showed a low resistivity on the order of 10^{-2} $\Omega \cdot$cm which is similar in the order of magnitudes from the literature data. [4,10] It is noted that the 20:1 and 30:1 AZO deposition show the highest carrier concentration and highest conductivity.
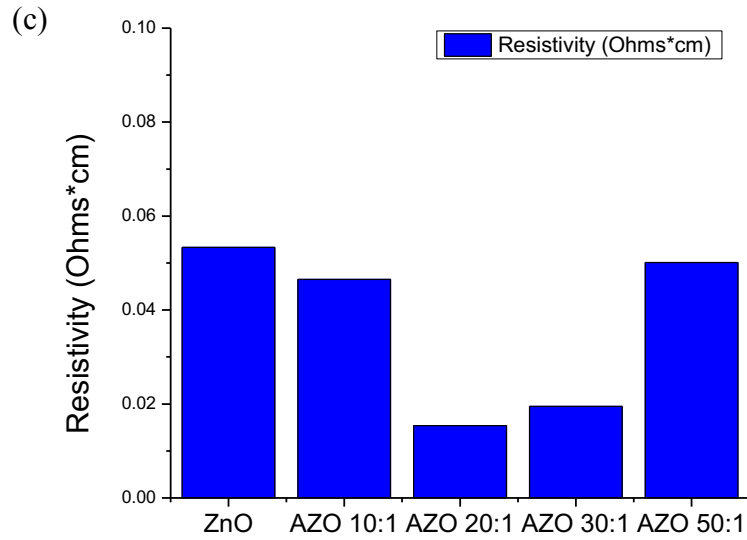
(a)

(b)

(c)
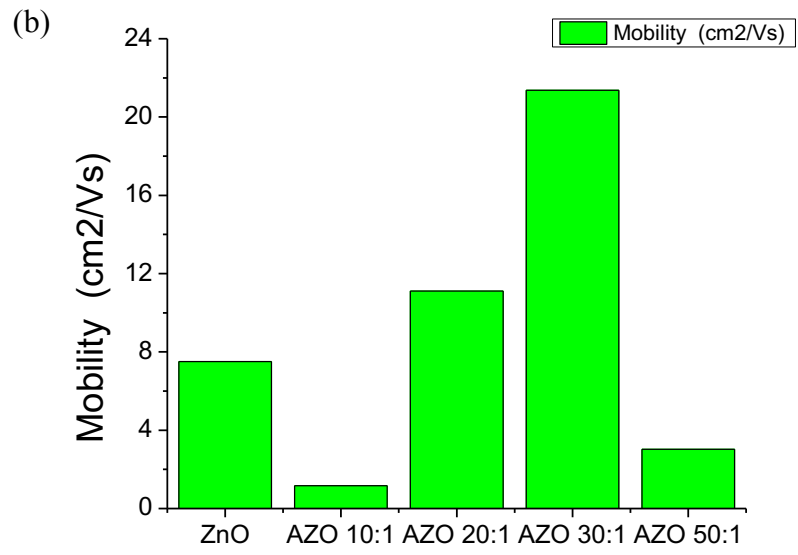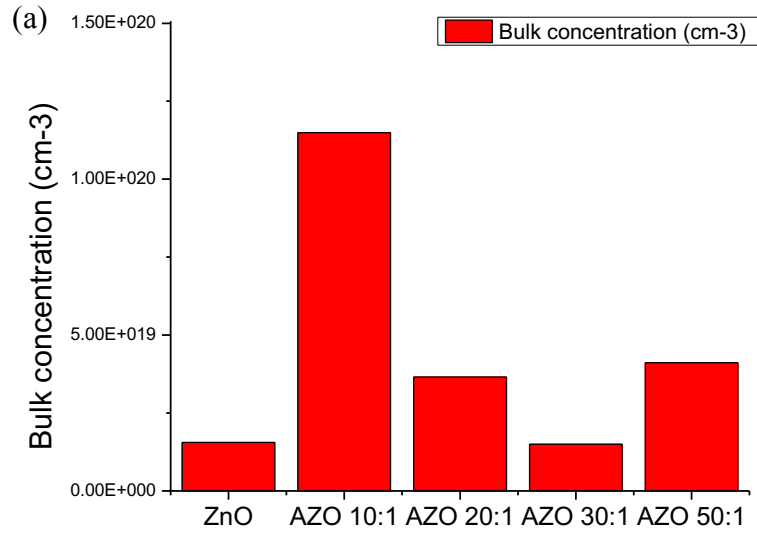
Fig. 5: Carrier concentration, mobility and resistivity extracted from Hall measurement

Name	Ratio	Cycles	Thickness (nm)	Bulk concentration	Mobility	Resistivity
ZnO	-	100	17.44	-1.56E+19	-7.5111	0.05333
AZO	10 / 1	154	21.08	-1.15E+20	-1.168	0.04652
AZO	20 / 1	147	24.38	-3.65E+19	-11.109	0.01538
AZO	30 / 1	155	24.53	-1.50E+19	-21.372	0.01947
AZO	40 / 1	164	10.79	N/A	N/A	N/A
AZO	50 / 1	153	25.24	-4.12E+19	-3.0254	0.05012

Table 3: ZnO and AZO carrier concentration, mobility and resistivity

4. Conclusion

To summary, we have illustrated that ALD can deposit a uniform AZO film. XPS results show that dopant concentration Al increases when decreases in the cycle ratio between Zinc and Aluminum precursors. Hall measurement illustrates that all of AZO are n-type based on measured bulk concentrations. Although hall measurement values are on the same order of magnitudes compared to the literature values, some of trends such as resistivity and mobility, for example, are offset a little bit which might due to the difference in growth conditions, operating cycles, and analyzing tools.

5. Appendix

Pressure monitoring study was conducted to increase the uniformity of the film and to investigate the possible reason about why 40:1 AZO shows an unexpected result.

1. Pressure monitoring – Unstable base pressure and strong H_2O pressure peak

The pressure to AZO growth time of 10:1 AZO and ZnO are shown in fig. 6 (a) and (b), respectively. Fig. 6 (a) demonstrates that the base pressure keeps increasing from 0.635Torr to 0.665Torr along with the operation time, and fig. 3 (b) depicts a strong H_2O pressure peak at around 5500s, followed by the base pressure shift upward. These two pressure behaviors happened several times on our operations that might affect the uniformity of the ZnO and AZO films, and we have proposed several possible reasons and solutions to target this issue.

First, clogged exhaust gas line is one of possible reasons that may lead the pressure spike. It is possible that not all of pulsed Zn and water precursor are completely reacted on top of the substrate. Once Zn precursor contacts with water precursor in the hot environment, they can react and form ZnO. If those ZnO are formed in the exhaust gas line instead of chamber because of the residue of the precursors, those ZnO may block the exhaust line, which may lead those abnormal pressures as discussed before. In order to alleviate this problem, we increased the purging time of H_2O from 25s to 45s to completely remove the water residue. Although pressure instability is mitigated, pressure perturbation still occurs. Therefore, increasing the purging time of H_2O further will continue to alleviate the problem. But the trade–off is longer processing time. In addition to clogged exhaust gas line, the second expected reason is the pressure sensor issue. If necessary, the pressure sensor need to be checked for more accurate experiments.
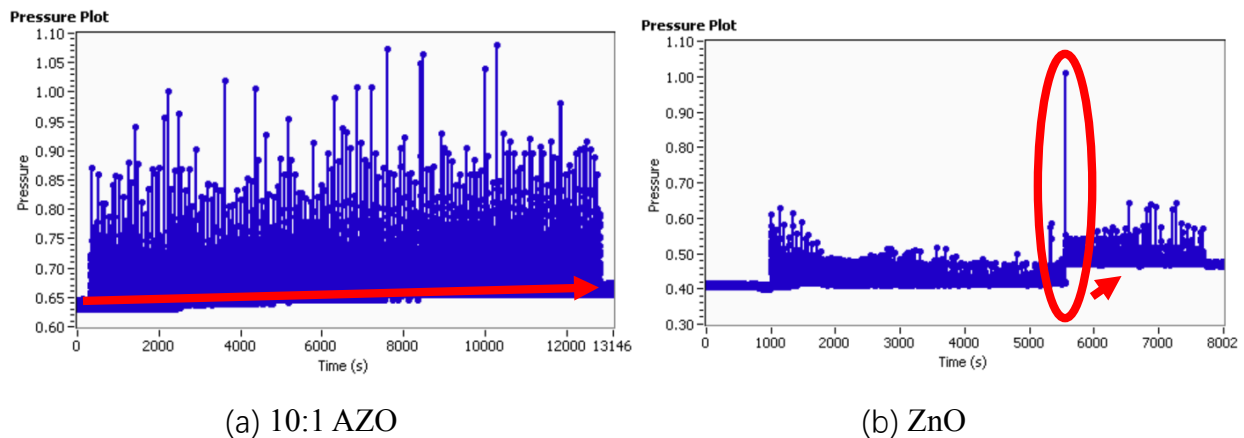

(a) 10:1 AZO   (b) ZnO

Fig.6: Pressure – operation time

## 2. Pressure monitoring – Weak Zn pressure peak

As discussed before, 40:1 AZO shows an unexpected growth compared to the other films. We assumed that the lower growth rate of 40:1 AZO is from the depletion of the Zn precursor. To

assure that our assumption, we have compared the pressure traces between 40:1 and 20:1 AZO, shown in Fig. 7. Fig. 7 (a) and (b) show the pressure pulses at the beginning and end of the 20:1 AZO deposition process, respectively whereas Fig.7 (c) and (d) show the beginning and end of the 40:1 AZO deposition process. Red arrows indicate Zn pressure peak. The Zn precursor injection pressure value of 40:1 AZO is around 0.01Torr, and Zn precursor injection pressure of 20:1 AZO is about 0.1Torr. There is 10 times reduction of Zn pressure in 40:1 AZO deposition process and this is a technical indication of the depletion of Zn precursor. To further examine the Zn precursor depletion possibility, additional ZnO deposition was operated and there was a huge thickness gradient on the same wafer (Fig. 8).
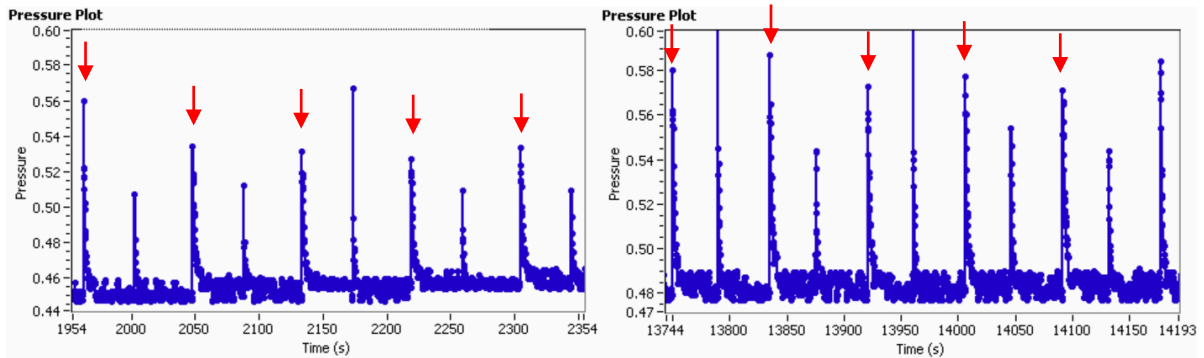
(a) 20:1 AZO beginning

(b) 20:1 AZO end
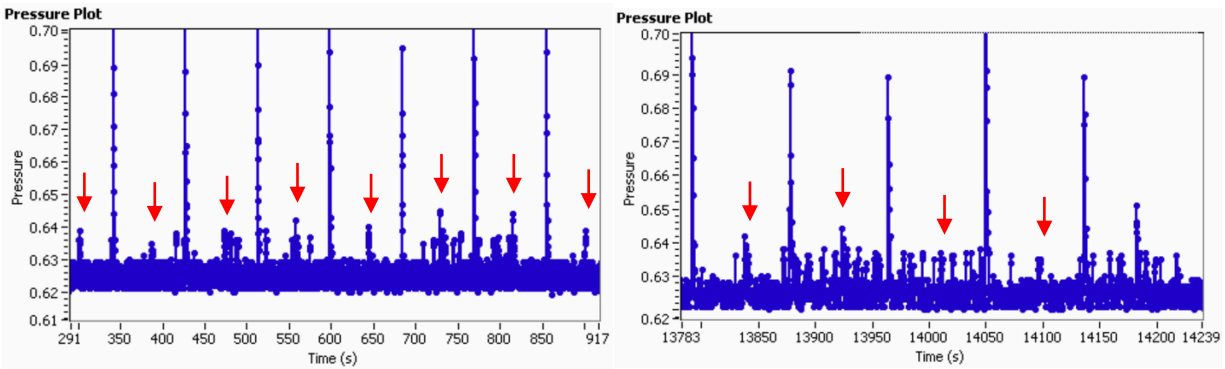
(c) 40:1 AZO beginning

(d) 40:1 AZO end

Fig.7: Pressure traces during AZO grow. x-axis refers to be the growth time, and y-axis is pressure
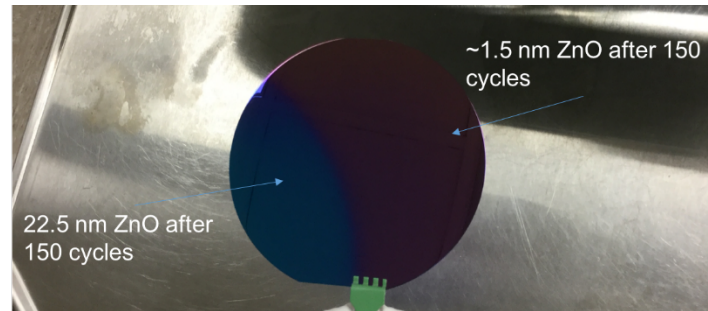
Fig.8: Thickness variation of ZnO on SiO$_2$/Si wafer due to the deficient Zn precursor

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