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Atomic Layer Deposition of TiO2 using Titanium Isopropoxide and H2O

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Abstract

Trials were carried out to deposit a film of Titanium dioxide (TiO2) by Atomic Layer Deposition (ALD) using Titanium Isopropoxide (TTIP) and H2O as precursors. Due to insufficient partial pressure, no coating was achieved. To increase the partial pressure, a bubbler was fabricated. TTIP was carefully filled in the bubbler, and deposition of TiO2 was obtained by a trial recipe. The number of ALD cycles was varied to obtain films of different thicknesses. The coatings were characterized using Ellipsometry, UV-Vis-NIR Spectrometer, and SEM-EDX [1].

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Introduction

Nanoscale technology is being developed at an accelerated rate in this era. Nanoparticles are being synthesized through various different techniques, but the major problem faced is of separating the nanoparticles from the solution. ALD can be used to achieve atomic-level film deposition; Intact nanoparticles are obtained in film form. ALD involves the separate chemical injection of gaseous phase precursors. ALD is performed at low temperatures (< 400°C) in contrast to CVD (Chemical Vapour Deposition) technique; hence degradation of nanometer-scale devices due to thermal diffusion is prevented. There are many other advantages associated with ALD, such as low impurity content, high aspect ratio, and step coverage close to 100%, pin-hole free deposition, and films are of excellent conformity.

Titanium dioxide (TiO2) thin films can be deposited using the ALD technique. TiO2 is a material that has been widely investigated for use in diverse applications such as photocatalysts in water purification, optical coatings [2], and high permittivity dielectric layers for gate oxides [3]. TiO2 is used for applications such as dynamic random access memory (DRAM) [4, 5] and ferroelectric random access memory (FeRAM) [6]. There is a range of titanium precursors, which include titanium tetrachloride (TiCl4) [7], tetrakis(dimethyl- amido) titanium (TDMAT) [8], and titanium isopro-poxide (TTIP). By product obtained by using TiCl4 precursor are corrosive, and there can be possible chlorine residues in the films [8]. TTIP, which is an alkoxide of titanium having a chemical formula of Ti(OCH(CH3)2)4, can be considered an appropriate precursor for TiO2 films because it has high vapor pressure [9]. It also exhibits non-corrosive and self-limiting growth, and high purity thin films are obtained. Significant decomposition occurs at lower deposition temperatures leading to an undistinguished ALD temperature window [10]. A conclusion can thus be drawn that TDMAT is the most appropriate precursor for depositing TiO2 using ALD [10]. However, in this work, deposition is done using TTIP.

In this paper, the working principle of the ALD technique is first explained, along with the chemistry involved for TiO2 deposition. The trials we conducted are described in detail leading to the fabrication of bubbler and filling of TTIP precursor in it. Subsequently, how to operate the equipment and deposit TiO2 thin films using TTIP as the Ti precursor in bubbler and H2O as the other precursor (known as the reactant or oxidant) is described. ALD growth was confirmed using ellipsometry. TiO2 layer was confirmed using EDX. Further UV-Vis-NIR Spectrometer and ellipsometry were used to study the optical properties of the deposited film. Growth per Cycle (GPC) as a function of the Number of Cycles is calculated. Suggestions are given for optimizing the recipe based on results obtained.

Experimental

Operational principle of ALD

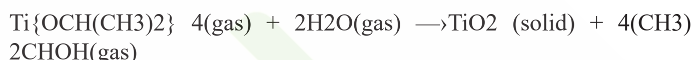
ALD is a chemical deposition technique that enables the formation of an atomic-scale thin film using the sequential reactions of separately injected chemicals. During the ALD deposition process, chemicals in their gaseous phases, known as precursors, are injected separately into the reactor of the ALD equipment.

Subsequently, each of them interacts with and is adsorbed onto the substrate surface, on which thin films are grown layer-by-layer.

Specifically, two precursors are used (denoted as A and B). Initially, precursor A is injected into the reactor. It will get chemisorbed onto the substrate surface, and then, by supplying a sufficient amount of inert gas, such as N2 or Ar, the precursor is degassed from the reactor (so-called 'purging'). Subsequently, precursor B is injected, and an identical method to that of precursor A is followed. Herein, it is important to separate the supply of precursor A from that of precursor B by degassing (purging) the remnant reactants for a specific period of time to prevent the reactants from interacting. This mechanism is known as a self-limiting reaction, which is characteristic of the ALD process. It is noteworthy that the sequential process involving the injection and purging of precursor A/precursor B is performed in a cycle, and this cycle is repeated as many times as required to deposit an atomistic thin film.

Chemistry involved for TiO2 deposition

Reaction:



Ti{OCH(CH3)2} 4(gas) + 2H2O(gas) ⟶TiO2 (solid) + 4(CH3) 2CHOH(gas)

In Figure 2, initially, there are hydroxide terminations on the surface. When TTIP is pulsed, the Hydrogen from OH termination reacts with OCH(CH3)2 and Ti{OCH(CH3)2} 3 gets chemisorbed on the Oxygen of OH termination. Then Nitrogen gas is purged in the reactor. This completes a sub-cycle of ALD deposition. Now Water i.e., the second precursor, is pulsed in the reactor. The Hydrogen in water reacts with OCH(CH3)2 and OH group is chemisorbed on Ti. This gives an OH termination at surface for initiation of next step. Now the N2 gas is purged, and this completes the entire ALD cycle.

Trials for deposition of TiO2

The deposition was done with 'HHV ALD 150' thermal ALD equipment, shown in Figure 1.a. TTIP precursor bought from 'STREM' was transferred to a precursor bottle. This precursor bottle was heated using a fiberglass tape heater, as shown in Figure 3, to get appropriate vapor pressure. The ALD pneumatic valves were used to pulse precursors in the reactor. An MFC is used for N2 gas as a carrier gas and for purging.

Valve manifold was maintained at high temperatures to avoid the condensation of the precursor. Also, the Trap and the Gas line were heated for the same purpose. A digital Pirani gauge was used to measure the pressure in the reactor.

Recipe: The precursor bottle was heated at 40°C, and the substrate heater was heated to 150°C (i.e., deposition temperature was 150°C). MFC was set at 20 sccm. The TTIP was pulsed for 1 sec and purging for 15 sec and water was pulsed for 0.2 sec, and purging was done for 15 sec.

The partial pressure of TTIP achieved was 0.005mbar, which was not sufficient for the deposition. Then the temperature of the precursor was increased in steps of 3°C up to 50°C, but the partial pressure achieved was increased to 0.085mbar.

As the temperature was increased to 63°C, the partial pressure dropped to 0.03mbar. For this trial, the deposition temperature was 200°C, and MFC was set to 15 sccm. Also, TTIP pulse time was increased to 1.5 sec.

No deposition was observed for the above trial recipes. The decomposition temperature of TTIP is 275°C [11], and further increase in deposition temperature would lead to non-linear growth of TiO2 as a function of a number of cycles. This led us to the conclusion that to increase the partial pressure without decomposition of the precursor, a bubbler is needed [12].

Fabrication of the bubbler

A bubbler for 100cc was designed as in Figure 4. The Bubbler was fabricated using a 42 O.D. (outer diameter) pipe with a thickness of 3.0mm.

Filling the bubbler

TTIP reacts in moisture to deposit titanium dioxide, thus TTIP could not be transferred in the fabricated bubbler in the ambient atmosphere. TTIP could easily be transferred into a glove box or glove bag. But due to their inaccessibility; a 'T' was fabricated as shown in Figure 7. One end of the 'T' was connected to the rotary pump for evacuation of bubbler and connecting lines. The other ends were connected to the precursor bottle and bubbler, respectively. Swagelok Manual Valves were used for isolation purposes. The precursor bottle was heated with a hot air gun to facilitate the transfer of precursor. After filling the bubbler, the 'T' was disconnected, and the outlet tube was connected to Swagelok manual valve and the ALD valve as in Figure 10.

Deposition of TiO2 thin film

- The silicon surface is blown off by Argon gas to remove any particles sticking on the surface.
- Pipelines are heated to avoid any condensation of TTIP.
- N2 gas of purity of 99.99% is used as the carrier gas at 20 sccm and is also passed through TTIP bubbler.

The Silicon wafer shown is Figure 11 has a crystal axis <100>, which made it convenient to cut the wafer into small rectangular pieces for deposition trials.

The vacuum was created in the reactor by 'HHV FD 20 Rotary Pump'. For opening the lid of the reactor, which was under vacuum for loading/unloading, the reactor had to be heated and then vented to avoid damage to O-ring.

Initially, the heating was started, and the reactor was vented for loading the substrates.

The reactor schematic was as in Figure 12 to quantitatively reduce the substrate use. During the trial, the silicon and glass substrates were placed as in Figure 13. The Trial recipe used is given in Tables 2 and 3.

When the said temperatures in Table 3 were reached, the recipe was initiated. The inlet tube of the bubbler was connected to the N2 gas through an ALD valve; the N2 was purged in the TTIP precursor by opening the rightmost ALD valve and a needle valve (not visible in Figure 10); connected for controlling the flow of N2 (due to unavailability of an MFC). The leftmost ALD valve in Figure 10 was also opened simultaneously; through this valve, the TTIP is pulsed in the reactor carried with N2 gas. Then the reactor was degassed by purging only N2 through the reactor through an MFC. Then 2nd valve from the right is opened for water pulse; however, N2 is purged continuously in the reactor. The Pressure Graph output (as in Graph was observed on the software of Figure 1.b; the needle valves attached to the precursor Bottle and bubbler were adjusted for sufficient partial pressures to achieve deposition. However, Swagelok manual valves were connected on the output tube of the bubbler and H2O precursor bottle before the ALD valve for the purpose of isolation of the precursor when not in use and during replacements. The recipe given in Table 2 was run for 1000 cycles with 5 substrates. The reactor was vented, and more substrates along with glass substrates were loaded, and the lid was closed and the vacuum was created inside the reactor, and N2 was purged continuously. When the temperatures as in Table 3 were reached, the equipment was initiated for another 500 cycles. The reactor was vented, and few samples were unloaded that had undergone 500, and 1500 cycles. The ALD equipment was set for another 500 cycles. After the above mentioned steps; samples with 500, 1000, 1500, and 2000 cycles were achieved. Also, some other depositions were done varying the deposition temperature. After the deposition was completed, the manual valves of the precursors were closed. The reactor lid was closed, and N2 was purged for some time for degassing the pipelines.

Results and Discussion

- Ellipsometry was used to measure the thickness of the film deposited. The samples tested were silicon substrates deposited for 500, 1000, 1500, 2000 cycles with a recipe of Tables 2 and 3.

The results obtained for thickness are plotted in Graph 2. We see that the plot is a straight line; this confirms that the deposition is of Atomic type.

The ALD growth was thus confirmed; this approved the test recipe developed. However this does not confirm that the recipe used was optimum but was a great start towards optimizing the recipe.

Growth Rate/Growth per Cycle (GPC) was calculated from the ellipsometry thickness data, which was around 0.2 A^o/Cycle, which is quite low. This indicated that the recipe needs to be optimized for having a higher GPC; the deposition temperature can be increased to 250°C [13]. Graph 3 shows that GPC decreases with a number of cycles. To avoid the decrease and maintain a high GPC, the recipe can be modified, and more doses of each precursor can be given [14].

- Ellipsometry was also used for measuring the refractive index of the deposited film. Refractive index was studied for the wavelength range of 400nm to 800nm. Graph 4 shows the variation of refractive index with wavelength for 40.53nm, 31.05, 21.01, and 12.81 thickness layers deposited on Si Substrate. We can see that towards the ultraviolet region, the refractive index increases; this can be used in applications like UV blocking, UV protective coating [15]. The refractive index at 500nm for the 40.53nm thick layer is measured to be 2.37. The refractive index matches with the data provided by Thomas Siefke [16]. The refractive index for the thinner layer is lesser than for the thicker one (although the trend is maintained); the reason for this being that the refractive index property depends on the crystal size, and thus for the thinner layer, the property is different from that for bulk [17].

SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray Analysis) confirms the presence of TiO2 layer. The Si substrate deposited for 500 cycles with the recipe of Tables 2 & 3 was tested. Figure 15 shows the peaks obtained through EDX where carbon was detected since carbon is a most likely contaminant in EDX analysis of surface composition. Even just the room air is a source of carbon contamination. Also, we can see that Ti:O composition ratio is not 1:2 in Table 5 as expected but the content of oxygen is much higher. The excess oxygen signal in EDX could originate from organic contamination. The contaminants' contents detected through EDX are quite high since the film thickness is very less of only 12.81nm. Ti detected at 4.55keV may be due to the Ti coated at the backside as more energy is needed to detect it. The Si was also detected in SEM-EDX, which is obvious as the substrate was of Si. The probe current in SEM was adjusted to get appropriate composition data.

UV-Vis-NIR Spectrometer was used to characterize the TiO2 film for transmission of E-M radiation in the wavelength range of 300nm-800nm. Glass sample, which was coated with 21.01nm layer of TiO2, was used as the sample. The transmittance of the bare glass sample was

also measured for comparison. In Graph 4 we see that the transmittance of bare glass and TiO2 coated do not differ much for visible range of spectra, especially for higher wavelength i.e., towards the infrared side. But still, some transmittance drop exists, which can be increased by increasing the film thickness and can be used for energy-saving window applications [18]. For the UV region, say at a wavelength of 305nm, the transmittance is seen to drop to 8% for deposition of 21.01nm thick layer of TiO2 on glass the compared to 24% transmittance through the bare glass. This can further be reduced by increasing the thickness of the film [18].
Hence TiO2 can be used as a UV- protective coating [14].

Future Scope

a. Optimize the parameters for increasing GPC.

b. Use TDMAT instead of TiO2 as Ti precursor and optimize the parameters for deposition of TiO2 as GPC with TDMAT precursor is higher than with TTIP [10].

c. Use Ozone as Oxygen precursor instead of H20, as the H2O-based ALD process brings impurities, such as hydroxyl groups (−OH) in the films [10].

d. To deposit TiO2 on Zeolite substrate and use for water purification [19].

e. To fabricate capacitor with TiO2 coatings and study it's dielectric properties [20].

f. Deposit TiO2 coating on optical devices for eliminating UV radiations [21].

g. TiO2 coating can be done for achieving TIR [22].

Conclusion

TiO2 film was successfully deposited by the ALD process, using TTIP and H2O as precursors, where TTIP was in the bubbler. The thickness of the TiO2 film was controlled by varying the number of cycles, and its deposition rate was estimated to be 0.2 Å/cycle, which could be increased by increasing the deposition temperature and a number of doses. The optical properties of the film were also studied

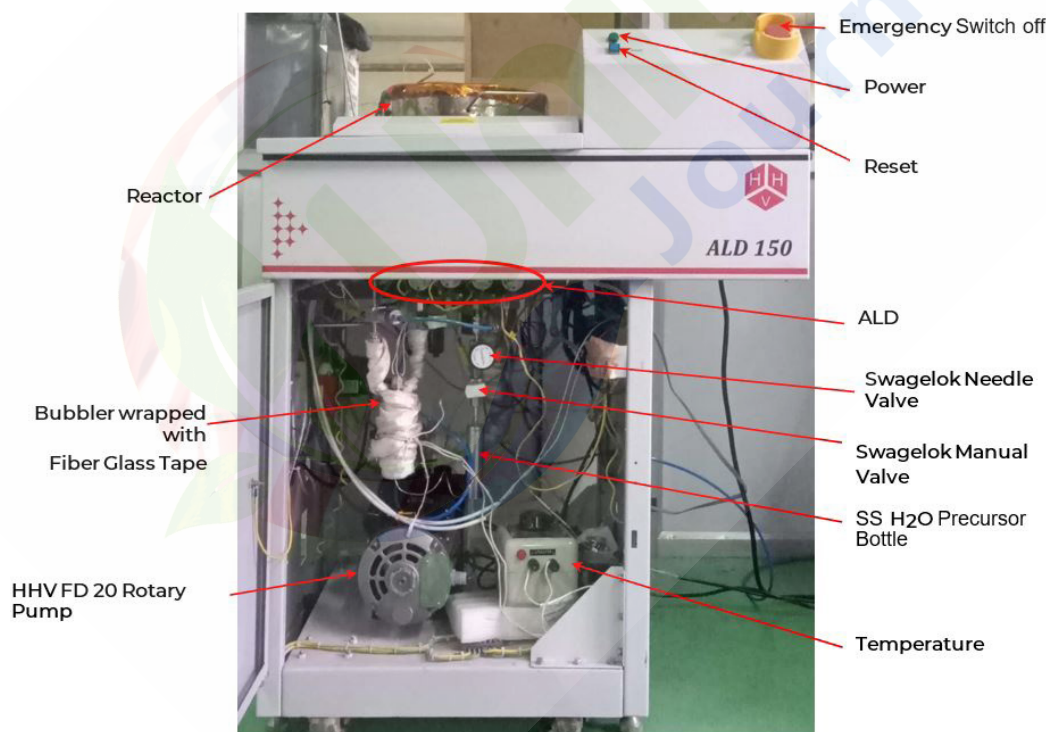


Figure 1.a: HHV ALD 150 - Thermal ALD Equipment

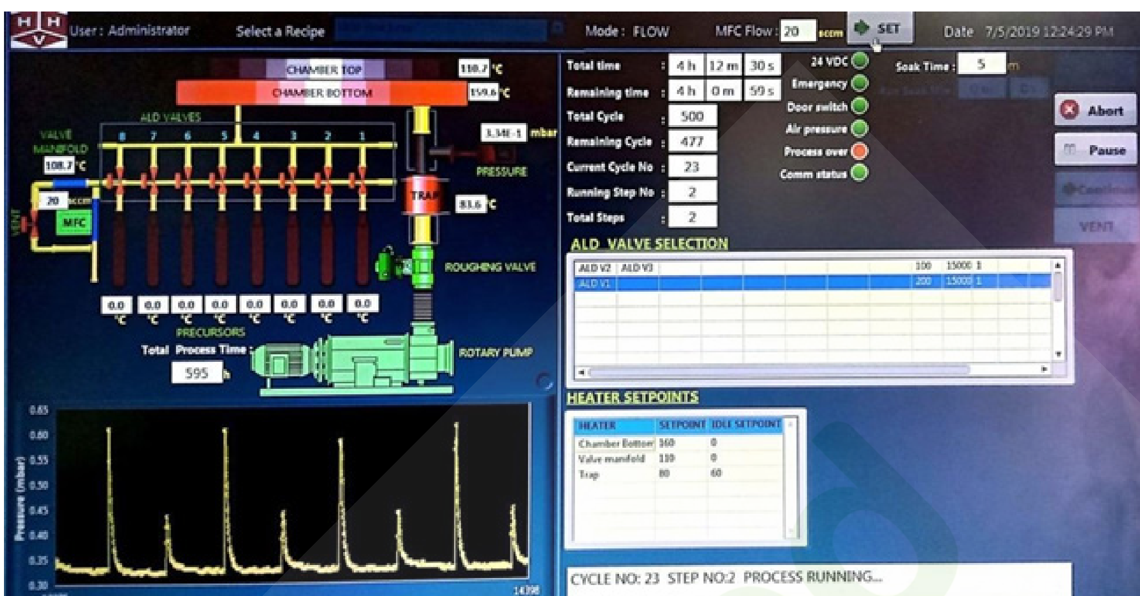


Figure 1.b: HHV ALD 150 Software

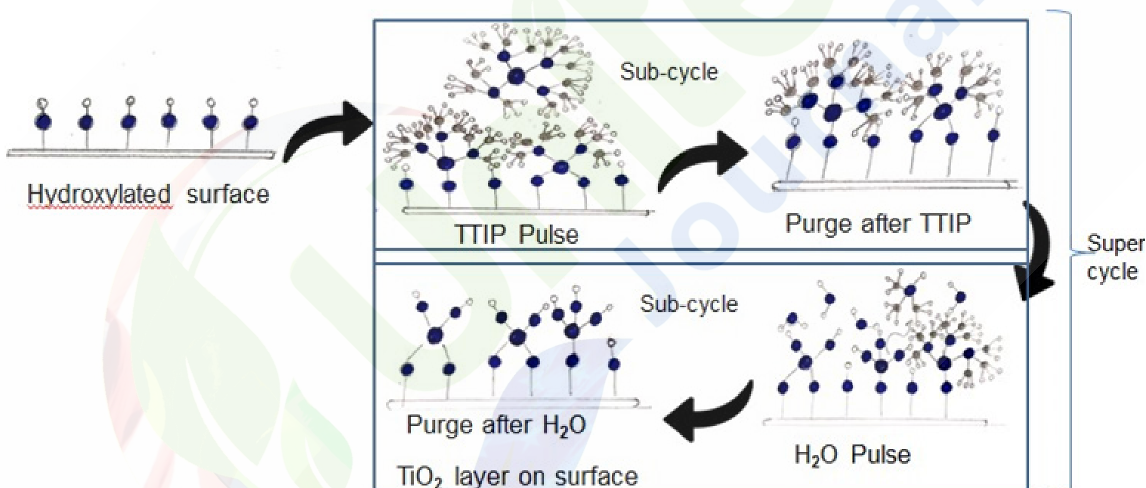


Figure 2: Reaction Analysis

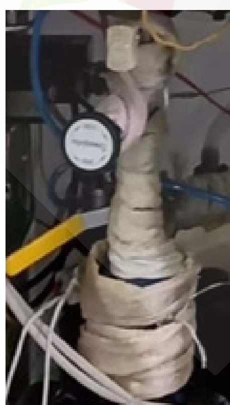


Figure 3: Precursor Bottle heated for getting vapours using Fiber Glass Tape Heater

Element	Symbol
Ti	●
O	•
	○

Table 1: Index

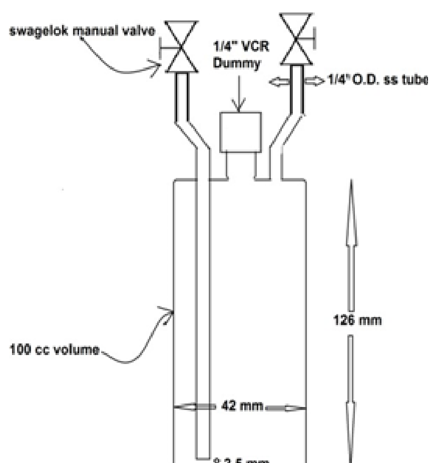


Figure 4: Bubbler Design

Figure 5: Male to Female Connector soldered

Figure 6: Swagelok Port Connectors Welded at Input-Output Tubes

Figure 7: 'T' Connected

Figure 8: Evacuating the 'T' Using the Rotary Pump

Figure 9: Hot-Air Gun Used to Transfer the Precursor in Fabricated Bubbler

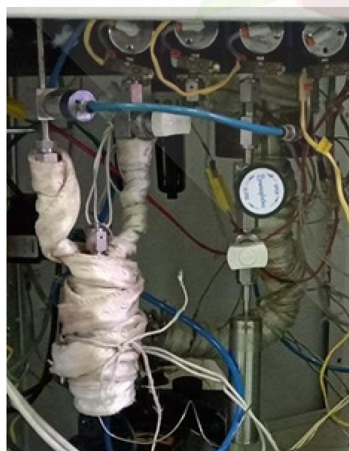


Figure 10: Bubbler is heated using the Fiber Glass Tape Heater. H2O is filled in S-S Precursor and is connected to the 2nd ALD Valve from right. Left Tube (inlet tube) of the Bubbler is connected to Rightmost ALD Valve (Used for Controlling the Flow of N2 gas).
Right Tube (outlet tube) of the Bubbler is connected to the Leftmost ALD Valve (Used for pulsing TTIP carried with N2 in the Reactor).

Figure 11: Hot-Air Gun Used to Transfer the Precursor in Fabricated Bubbler

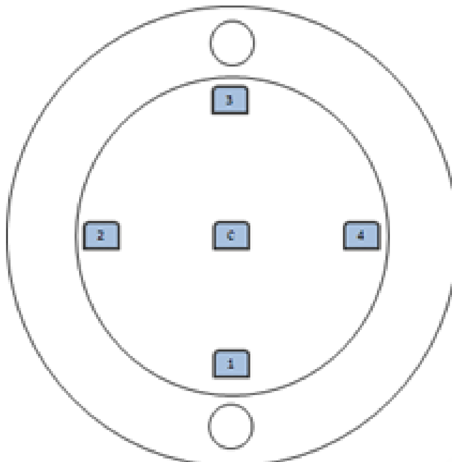


Figure 12: Reactor Bottom and Sample Positions

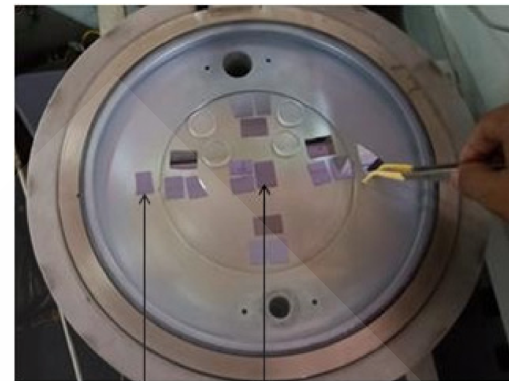


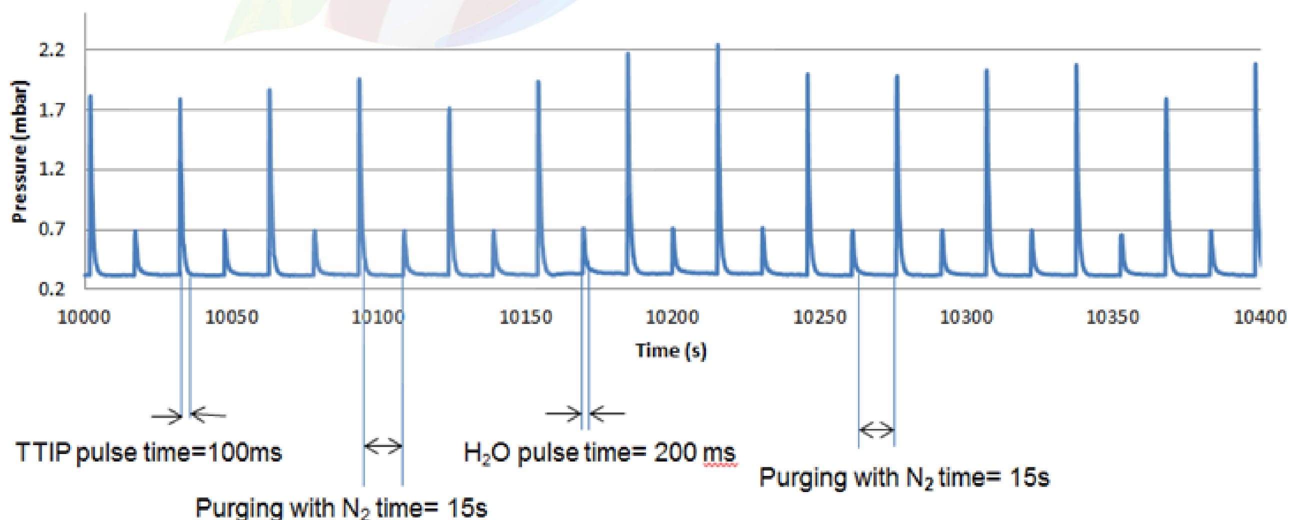
Figure 14: Unloading Sample

Table 2: Pulse and Purge Time of Precursors

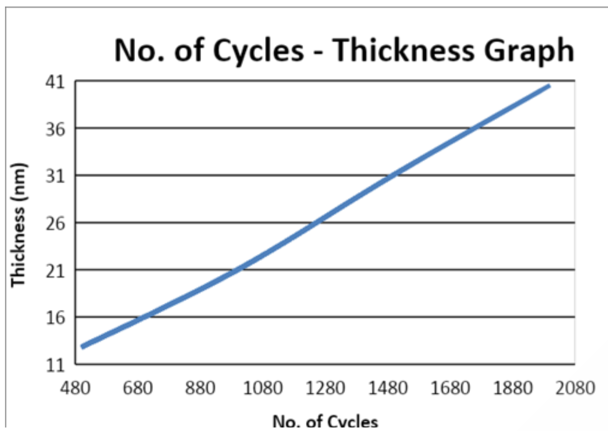
Precursor	Pulse Time(ms)	Purge Time(s)	Dose
TTIP	100	15	1
H_2O	200	15	1

Table 3: Temperature Specifications

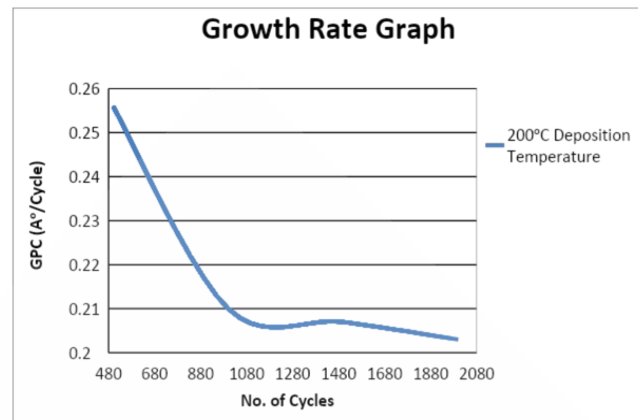
Heater	Temperature(°C)
Bubbler	55
Valve Manifold	110
Trap	90
Substrate Heater	200
Vacuum Heater	80



Graph 1: Pressure Changes in the Reactor



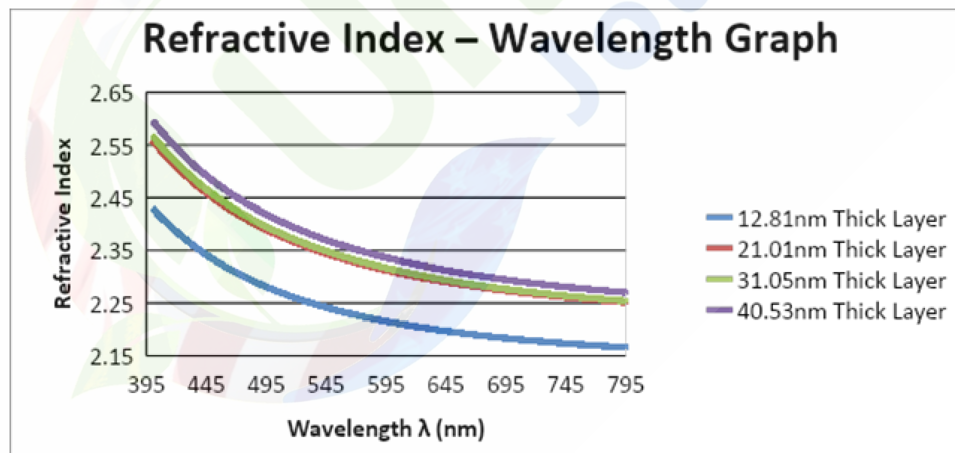
Graph 1: Thickness Plot against No. of Cycles



Graph 2: GPC for TiO2 Film as a Function of No. of Cycle

No. of Cycles	Thicknes s	Growth per Cycle (A°/Cycle)
500	12.81	0.256
1000	21.01	0.210
1500	31.05	0.207
2000	40.53	0.203

Table 4: Ellipsometry Data



Graph 3: Refractive Index as a Function of Wavelength for a Range of TiO2 Film Thickness

Element	Weight %	Atomic %
Ti	0.71 +/- 0.06	0.34
O	7.54 +/- 0.25	10.94
C	11.57 +/- 0.54	22.38
Si	80.19 +/- 0.54	66.34
Total	100.00	100.00

Table 5: EDX Data

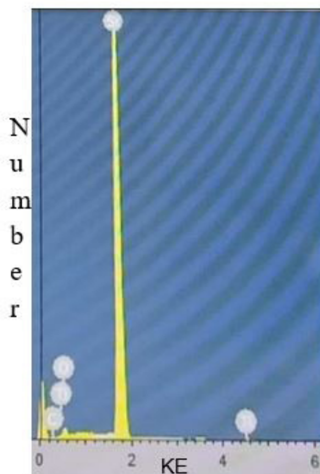
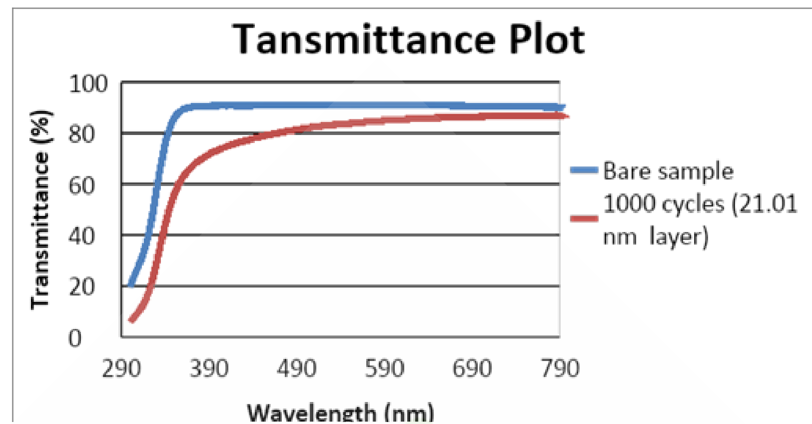


Figure 15: Composition Analysis



Graph 4: Changes in Tranmittance Property of Glass when coated with TiO2 Layer

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