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Atomic Layer Deposition

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1. Overview

Over the course of a semester, understanding of the theory and application of Atomic Layer Deposition [ALD] was pursued, all in preparation for further research focusing on the charge carrier type, density, and mobility in ultrathin film ZnO. At the beginning of the semester a wide array of scientific articles was read in order to build up a basic understanding of the processes at play, at which point hands on experience was acquired on the ALD system present in Parag Banerjee's lab. The following paper simply reflects the knowledge gained throughout this process as well as where that knowledge will be applied in future endeavors.

2. Theory

ALD exists as a subcategory within the larger group of deposition techniques known as Chemical Vapor Deposition [CVD], which relies on the premises of running gaseous substances over either a target substance or the substrate itself in order to facilitate deposition through surface reactions. Other CVD processes require plasma or high temperatures to provide the energy necessary to facilitate deposition, but ALD uses gases with a low kinetic barrier, i.e. they can occur at relatively low temperatures. This presents the question of how exactly does one have any control over the smoothness of the surface since this would seem to cause erratic nucleation all over the substrate surface as well as uncontrollable reaction speeds [1].

What further makes ALD unique within CVD, and the answer to the prior question, is that it employs sequential, self-limiting surface reactions, depositing single atom surface layers at a time, allowing for fine tune control over deposition rates and thicknesses. A typical ALD process will consist of two surface reactions to create a single layer of a binary compound. Not all ALD processes use a binary process with only two surface reactions, but most do, and the specific example focused on later does so it suffices for the discussion at hand. Figure 1 presents a more visual method of this process.

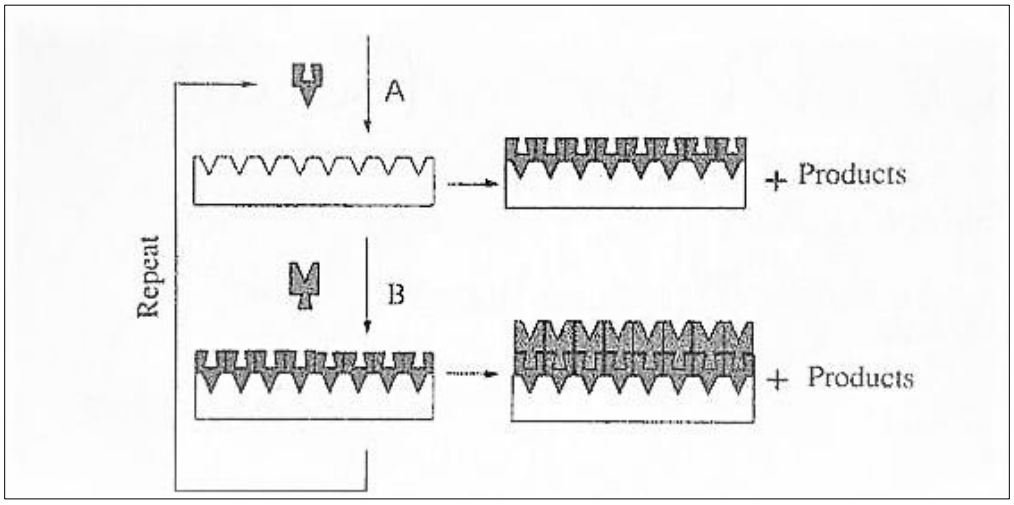

Fig 1. (op. cit. [2]) If we consider A to be the first gaseous substance, or precursor, it reacts with the surface substrate on a limited number of sites. Precursor B then undergoes a surface reaction with those sites, once again resulting in a finite number of new sites, with which precursor A will react. (Hence, the terms sequential and self-limiting) The final product of precursor A and B will be the binary compound desired.

In a more practical sense this plays out as two single 'pulses' of reactive gases separated by inert gas 'purges' to prevent the reactive gases from interacting with the substrate at the same time [2].

For example, in the case of ZnO being deposited on top of SiO_2, the two precursors would be diethyl zinc [DEZ], i.e. $Zn(C_2H_5)_2$, and water, i.e. H_2O [3]. The chemical processes that take place due to these precursors are shown in Fig 2.

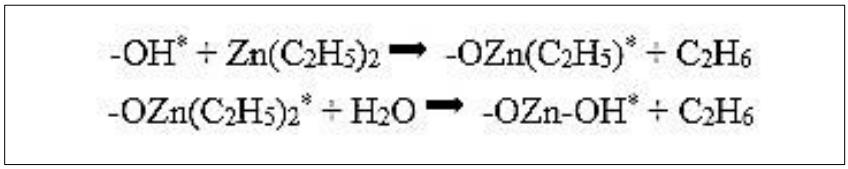

Fig 2. (op. cit. [3]) " * " denotes a current surface site, " - " being the connection to the rest of the surface from the presented elements. The -OZn-OH* is the equivalent of an -OH*, with the -OZn added to simply demonstrate that a layer of ZnO has been added that terminates in an OH, allowing the cycle to start all over again.

The initial -OH* group to start the entire process actually comes from silanol groups present on the surface of silica. Further considerations of this present dilemma lead to several realizations, in no specific order.

1. The chamber must be pumped to a low pressure before beginning to prevent contamination.
2. The precursors must run over the substrate for a sufficient enough time to react with all or almost all of the sites available on the surface to get near perfect deposition.
3. While the reaction has a low kinetic barrier, temperature will still play an important role in determining the speed at which reactions will occur and on the sticking coefficient of the oncoming precursors.
4. The pressure of the precursor will be important in considering the flux onto the substrate, as well as the pressures of any other gases present in considering potential contamination.
5. The purge gas cannot react with the substrate or either of the precursors, and must be pumped through the chamber long and/or quickly enough to get the remnants of each prior pulse of precursor out.

Now that an introductory foundation in ALD has been acquired, from the actual process to a brief consideration of various parameters at play, how does this actively play out in the lab in question?

3. Lab Work

The first issue with actually performing ALD is preparing your substrate sample. First, the wafer has to be cut to an appropriate size for the chamber in question, since the sample tray is fairly small. The sample is then placed in a glass beaker filled with isopropyl alcohol (IPA) and ultrasonic cleaning is performed for 5-10 min. This serves to vibrate the cleaning solution at a rather high frequency, in order create cavitation bubbles within the liquid, thereby causing any remaining contaminants on the surface to experience high forces of agitation. From there the

sample is rinsed in de-ionized water and dried with compressed air in order to remove any last remaining IPA and water. As an aside, the deionized water and air should flow almost parallel to the surface and in a consistent direction throughout this cleaning process in order to prevent the substrate from breaking and to prevent any liquid from simply moving in different directions along the surface without actually being removed, respectively. From there, depending on the experiment in question, the substrate can then undergo ozone cleaning in order to convert a substance from hydrophobic to hydrophilic, which can facilitate many processes, as can be seen in that even this one example of ZnO uses H_2O as a precursor. However, this step is not very important to the process at hand, ZnO, since silica is naturally hydrophilic until only silanol remains, which is exactly the natural limit needed to continue the cycle of deposition.

Now that the sample has been prepared, it is ready to be inserted into the ALD chamber. Figure 3 includes photos of the entire apparatus as well as labels of individual parts.

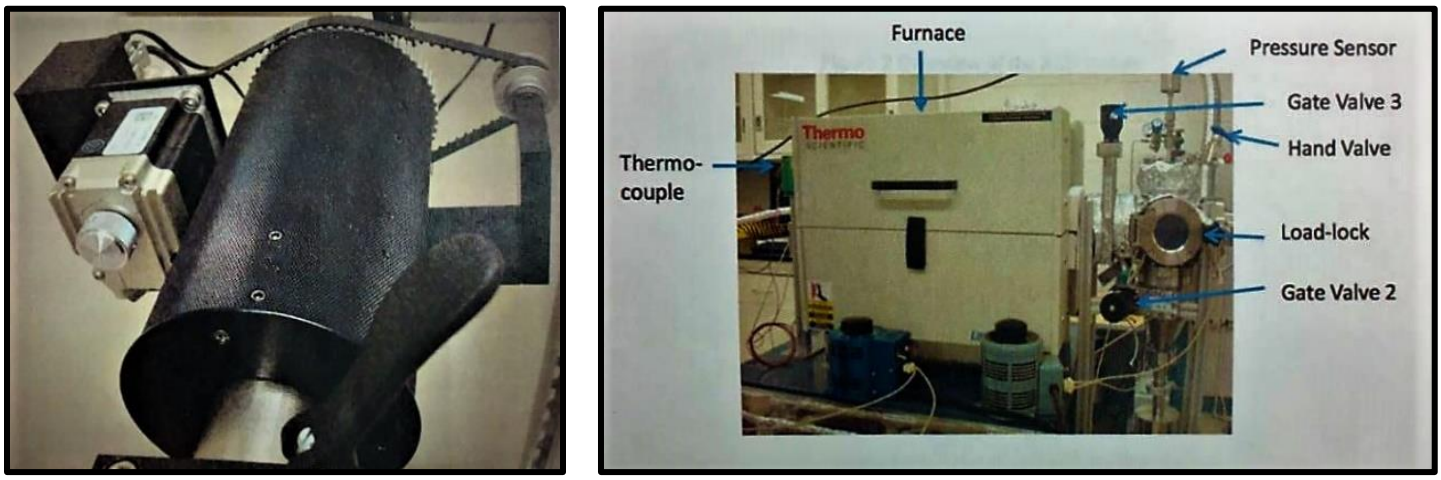

Fig. 3 (pulled from Lab Manual)
This first image is the Rotating Server Arm, while the second is the remaining components of the ALD system with its constituent parts labeled here.

The first step in getting the sample inside of the chamber and performing ALD, after putting the sample in the sample dish, is to open the load lock and, using cooking tongs to hold the sample dish on the lower left hand corner, slide the sample dish in and rotate it to slip onto the prong. There is a screwdriver provided to then tighten the sample dish in place – usually only half a turn is required here. At this point, the load lock can be lightly screwed shut – it will self-tighten as the inner chamber loses pressure. Now the hand valve can be closed, which prevents atmospheric pressure from entering the chamber. At this point the vacuum pump can be turned on, which will begin to pump the section contained by the hand valve and gate valves. Once the pressure in this segment begins to drop, one can open gate valve 3 to allow the pump to also pump air out of the furnace itself. The sample dish can be moved inside the chamber using the rotating server motor, where the sample will now be ready for deposition.

Before that can begin however, the pressure within the furnace has to drop sufficiently, and the temperature has to rise to about 120 C (varying depending on the process at hand), before a Labview program can be run to perform the ALD. The program controls which precursors and purge materials flow in, for how long, and at what flow rate. By then controlling how many cycles of this process occur, it becomes fairly easy to convert number of cycles to deposition height, allowing for, again, fine tune control of deposition thickness. After the program has run

its course and the ALD is finished, the exact same steps are followed, simply in reverse, making sure to open gates slowly if needed to prevent sudden changes in pressure within the ALD apparatus.

4. Future Goals

In the end, while this pursuit of knowledge is interesting of itself, what is the purpose? The student's study of Atomic Layer Deposition and how to use the chamber in Parag Banerjee's lab will become crucial to the creation of a device that allows one to take cold temperature Hall Measurement's on ultrathin film ZnO, primarily due to the fact that the ZnO will need to be ~5 nm in thickness. ALD reigns supreme in its ability to grow thin films with subnanometer resolution due to its self-limiting nature, making it perfect for this task. However, ALD is not the only step that will require training required for this device - tools such as Thermal Evaporation and Photolithography will also be at play in this device fabrication. Once understanding of these devices has also been achieved and a degree of confidence achieved, the Hall Measurement device will become a feasible piece of fabrication. Upon creation and subsequently acquiring of data, these Hall Measurements will allow further investigations and understanding into the carrier properties of thin film ZnO, which remain questionable at this time.

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[3] Gao, Zhengning, Fei Wu, Yoon Myung, Ruixiang Fei, Ravindra Kanjolia, Li Yang, and Parag Banerjee. "Standing and Sitting Adlayers in Atomic Layer Deposition of ZnO." Journal of Vacuum Science 34.1 (2016): n. pag. Print.