
Technology Backgrounder: Atomic Layer Deposition

Introduction

The following discussion is an excerpt from the forthcoming IC Knowledge publication “2004 IC Technology”.

As IC processes transition to 65nm and smaller linewidths there are three main thin film requirements that are driving the need for new deposition technologies:

- Gate dielectrics need to transition from silicon dioxide (or nitrided silicon dioxide) to high-k dielectric. High-k dielectric requires the ability to deposit very thin (a few nm) - well controlled films.
- DRAM capacitor dielectrics are already transitioning to high-k dielectrics. Once again the need exists to deposit very thin - well controlled films. DRAM capacitors also require filling of features with aspect ratios as high as 60:1 (depth to width ratio).
- Interconnect barrier layers are becoming thinner and the aspect ratios of the features the barriers are deposited into are also increasing.

Traditionally gate silicon dioxide has been thermally grown and then nitrided, DRAM capacitor dielectrics have been deposited by Chemical Vapor Deposition (CVD) and barrier films are deposited by Physical Vapor Deposition (PVD) or in some cases CVD. Problems with thickness control and uniformity generally limit CVD and PVD processes to films thicker than 10nm and 20nm respectively [1]. CVD processes only assure 100% step coverage on aspect ratios of approximately 10:1 and PVD processes only offer 50% step coverage even at 10:1 aspect ratios [1]. With thin film thickness requirements evolving to <10nm and aspect ratios for DRAM capacitors reaching 60:1, the need for new deposition technologies is apparent.

Atomic Layer Deposition Process

In a “standard” CVD process a wafer or a group of wafers are placed in a vacuum chamber where chemical vapors are thermally reacted at low pressure to deposit a film on the wafer. The deposition process is continuous - the vapors flow continually into the chamber during the deposition cycle. The deposited film thickness depends on the temperature, pressure, gas flows volumes and uniformity, chemical depletion effects and time (for state-of-the-art processes batch systems are generally no longer used due to the difficulty of achieving temperature and gas flow uniformity over multiple substrates at the same time). Controlling all of these parameters to the level required for good thickness control of thin films is very difficult.

Atomic Layer Deposition (ALD) deposits films using pulses of gas producing one atomic layer at a time. Within fairly wide process windows the deposited film thickness is only dependent on the number of deposition cycles providing extremely high uniformity and thickness control. The basic deposition process is illustrated in figure 1.

Figure 1 illustrates the deposition of zirconium dioxide. The deposition steps are:

1. $ZrCl_4$ vapor is introduced into the process chamber.
2. The $ZrCl_4$ vapor forms an adsorbed monolayer on the surface of the wafer. Although not shown, following monolayer formation the chamber would be purged of $ZrCl_4$ vapor by an inert gas prior to the next step.

3. H₂O vapor is introduced into the chamber.
4. The H₂O vapor reacts with the ZrCl₄ surface monolayer to produce one monolayer of ZrO₂. Because only a monolayer of ZrCl₄ exists on the wafer surface, only one monolayer of ZrO₂ is produced making the process self limited. Following ZrO₂ formation the chamber would be purged again and additional cycles would be performed as necessary to produce the desired film thickness.

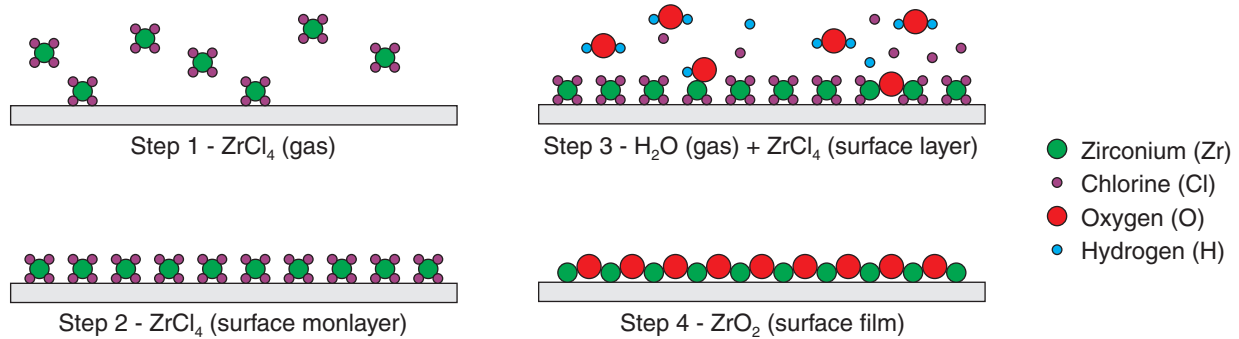


Figure 1. Atomic layer deposition of ZrO₂.

ALD reactions are typically carried out in the 200°C to 400°C temperature range. If the deposition temperature is too high, chemical bonding cannot be sustained or the density of chemically reactive sites is reduced - reducing deposition rates. If the deposition temperature is too low thermally activated chemisorption and film forming reaction rates decrease reducing deposition rates [2]. As the deposition temperature is increased from low to high the deposition rate increases - reaches a peak and then decreases. The temperature window for maximum deposition rate is relatively wide compared to CVD processes that are much more temperature sensitive. Figure 2 schematically illustrates the allowable temperature window for ALD.

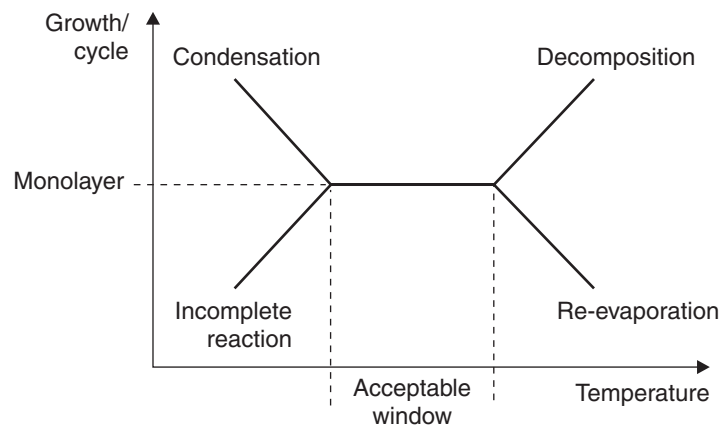


Figure 2. ALD acceptable temperature window.

Precursors must be volatile and thermally stable to ensure efficient transportation so that reactions will not be precursors transportation controlled. The vapor pressure of precursors must be high enough to completely fill the deposition chamber so that monolayer deposition takes place within a reasonable length of time (approximate vapor pressures of 0.1 torr). Precursors must chemisorb onto the surface or rapidly react with surface groups and react aggressively with each other to keep deposition times short. The precursors cannot self-decompose or the self limiting property of ALD is lost and the precursors shouldn't etch or dissolve into the film or substrate [3].

The following table - table 1, is taken from the IC Knowledge publication “Visual Guide to Semiconductor Process Equipment” and presents a list of films deposited by ALD with the precursor chemicals used, temperature and application. From table 1 the wide variety of films that can be deposited by ALD becomes apparent, and this is not a complete list.

Table 1. ALD films and applications.

Film	Precursors	Temperature °C	Application	Ref
Al ₂ O ₃	Al(CH ₃) ₃ , H ₂ O or O ₃		High-k dielectric	2
AlN				
Cu	CuCl, Cu(thd) ₂ or Cu(acac) ₂ with H ₂ , Cu(hfac) ₂ xH ₂ O with CH ₃ OH	360-410, 175-300, 250, 203-300	Interconnect	12,13, 14,15, 16
HfO ₂	HfCl ₄ or TEMA, H ₂ O		High-k dielectric	
Mo	MoF ₆ , MoCl ₅ or Mo(CO) ₆ with H ₂	200-500, 500-1100, 200-600		15
Ni	Ni(acac) ₂ , 2 step process NiO by O ₃ reduced afterwards by H ₂			12
SiO ₂	SiCl ₄ , H ₂ O		Dielectric	6
Ta	TaCl ₅ ,		Barrier	11
TaN	TBTDET, NH ₃	260	Barrier, deposited with plasma enhancement	8
TaO ₂				
Ti	TiCl ₄ , H ₂		Glue layer, deposited with plasma enhancement	11
TiN	TiCl ₄ or TiI ₄ , NH ₃	350 - 400	Barrier	5,7
TiO ₂			High-k dielectric	
TiSiN				
W	WF ₆ , B ₂ H ₆ or Si ₂ H ₆	300 - 350	Interconnect plug fill	9,10
WN			Barrier	
WN _x C _y	WF ₆ , NH ₃ , TEB (triethylboron)	300 - 350		3
ZrO ₂	ZrCl ₄ , H ₂ O		High-k dielectric	

Another interesting feature of ALD is the ability to create layered films one atomic layer at a time. HfO₂ (Hafnium dioxide) is a high-k film with a k value of 25 and it is now generally agreed that HfO₂ or some form of hafnium silicate in the form of HfSi_xO_y and HfSiON will be used as a replacement for silicon dioxide as a gate dielectric for sub 65nm linewidth devices. While HfO₂ has a higher k value than Al₂O₃, k = 25 versus k = 9, HfO₂ has a lower barrier height making it more prone to leakage. ALD can be used to produce a nanolaminate film of alternating layers of HfO₂ and Al₂O₃ producing a film with a higher k value than Al₂O₃ and a higher barrier than HfO₂. This approach is being used by Samsung for 90nm DRAM production [16].

The main draw backs to ALD are the relatively slow deposition rates compared to CVD and the need to perform frequent maintenance on the equipment. Figure 3 compares ALD step coverage and deposition rate to other deposition techniques.

The systems covered in figure 3 are:

- PVD - physical vapor deposition (sputtering).

- I-PVD - ionized physical vapor deposition. I-PVD improves PVD step coverage by collimating the arrival of the sputtered atoms at the wafer surface.
- CVD - chemical vapor deposition.
- PDL - pulsed deposition layer. An “ALD like” process that deposits multiple layers at once.
- ALD - atomic layer deposition.

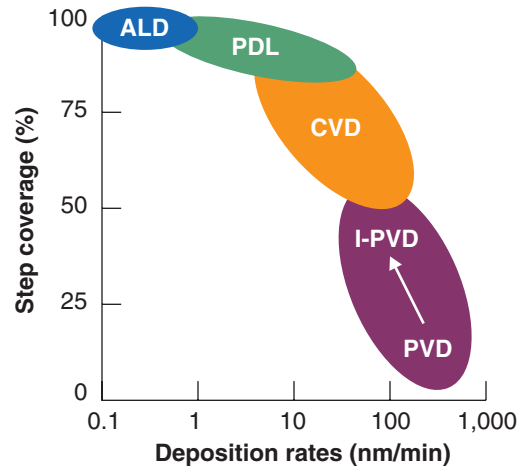


Figure 3. Step coverage and deposition rate versus deposition technique [1].

Note how improved step-coverage is gained at the expense of deposition rate.

ALD Systems

There are four main types of ALD reactors [3]:

- Closed system chambers - the reaction chamber walls are designed to effect the transport of the precursors.
- Open system chambers - the chamber is designed so that the walls do not effect the precursor transport - the chamber is very large relative to the wafer position.
- Semi-closed system chambers - a channel is formed by two wafers and the precursor is fed between the two wafers.
- Semi-open system chambers - similar to a semi-open systems except one side of the precursor channel is a wafer and the other side is gas limited.

A basic closed ALD system is illustrated in figure 4.

Key elements of the system illustrated in figure 4 are:

- Two controlled temperature liquid baths provide vapor to the system.
- Each of the liquid baths is isolated from the system by high actuation-speed valves. The valves turn on and off the precursor flows to the system providing the precursor vapor pulses.
- The wafer is held in the center of a low volume reaction chamber. For good throughput the chamber must purge quickly between each gas pulse.
- The reaction chamber is heated to initiate the surface reactions for film deposition.
- A vacuum pump maintains flow through the system and facilitates rapid purging of the precursor gases between cycles,

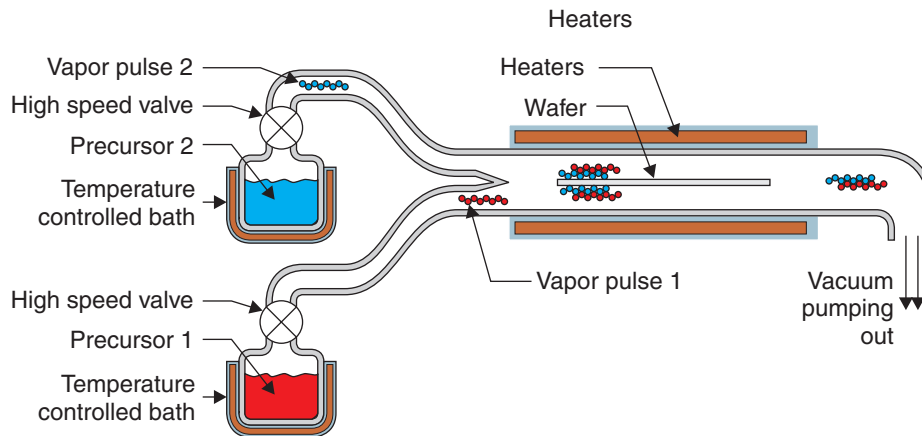


Figure 4. Atomic layer Deposition System.

In order to achieve high deposition rates with ALD, the system must be able to achieve rapid reactions during gas pulses and rapid purging in between gas pulses (cycle times are on the order of 1 to 10 seconds [19]). Rapid purging requires high purge gas flows but in order to maintain a stable pressure in the system the same total volume of gas needs to flow during deposition and purge. Low vapor pressures for precursors used in ALD means that the precursor gas pulses are typically diluted with an inert carrier gas to achieve the required gas flow rates. Dilution reduces the reactivity of the pre-cursors lengthening reaction times and carrying unreacted precursor into the pump wasting precursor and increasing the need for system maintenance.

There are a variety of approaches being pursued to improve productivity of ALD systems.

- Batch systems - conceptually the simplest approach to improving ALD productivity is to deposit films on more than one wafer at a time. Since ALD has a relatively wide temperature window and is not gas flow dependent as long as the chamber is saturated with precursor, multi-wafer designs with good uniformity are practical.
- Plasma Enhanced ALD - uses a plasma to accelerate the deposition reaction during ALD. Figure 5 illustrates a plasma enhanced ALD reactor based on Genitech's design [20].

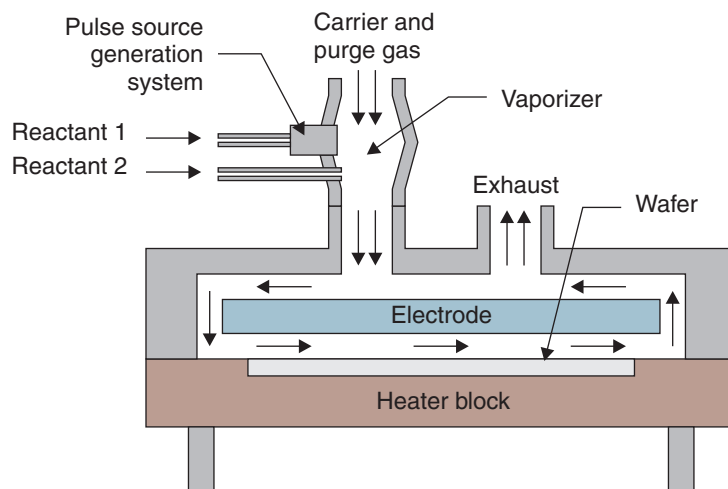


Figure 5. Plasma enhanced ALD reactor. Adapted from [20].

Note the addition of the plasma electrode above the wafer in the system illustrated in figure 5.

- Improved chemical delivery - Sundew Systems has developed an alternate chemical delivery and gas flow system that delivers precursors to the process chamber at low flows undiluted improving reaction time and efficiency and maintains system pressure by delivering a flow of inert gas into the pumping system after the reaction chamber [21]. The combination of the precursor flow and inert gas delivered directly to the pump is the same total flow as the high flow purge gas so that chamber pressures are maintained during both deposition and purge cycles. Figure 6 illustrates the system.

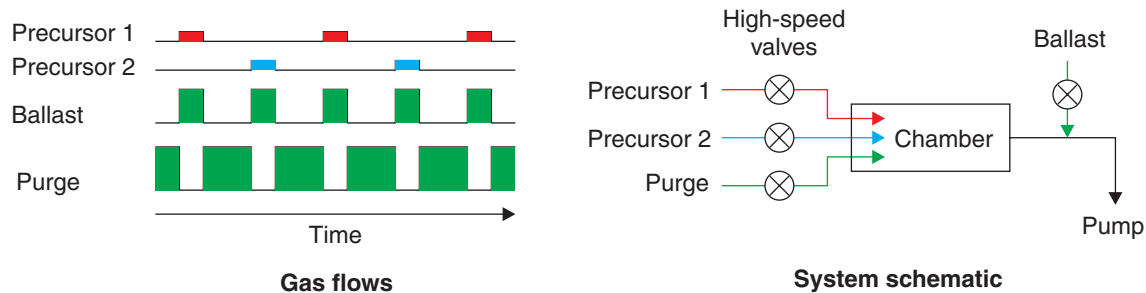


Figure 6. Sundew Technology - high productivity ALD approach.

Conclusion

There is no question that ALD will be a critical technology for future generation ICs. A key differentiating factor for ALD suppliers will be the ability to drive up productivity and drive down cost of ownership. To learn more about state-of-the-art IC process technology we recommend the IC Knowledge - 2004 IC Technology publication due out in August 2004. This discussion is an excerpt from that publication.

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