

## Applications of Atomic Layer Chemical Vapor Deposition for the Processing of Nanolaminate Structures

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**Abstract**—Atomic layer chemical vapor deposition (ALCVD) is a variant of a CVD process that involves surface deposition for the controlled growth of nano-thickness films. ALCVD is based on the self-limiting surface reaction with less than a monolayer chemisorption of chemical precursors. Advantages of the ALCVD process are uniform film growth on large area substrate, easy control of composition in atomic level, low growth temperature, multi-layer thin film growth with various composition, and wide process window. Since initially developed by Suntola in 1977, ALCVD has been used for the growth of various materials, including oxides, nitrides, metals, elements, and compound semiconductors. This article reviews the basic principle, mechanism, characteristics, and applications of ALCVD.

Key words: Atomic Layer Chemical Vapor Deposition, Self-limiting Chemisorption, Nano-Deposition, Gate Oxide, Capacitor Dielectric Thin Film

### INTRODUCTION

#### 1. Previous History and Current Status

Atomic layer chemical vapor deposition (ALCVD), which is based on the controlled growth of thin films, has attracted much attention as an advanced materials processing for nano-thickness thin film deposition [Haukka et al., 1997; Suntola, 1996; George et al., 1996; Ritala et al., 1999]. ALCVD was first developed in 1977 by Suntola et al. for the growth of ZnS : Mn thin films. The original application of ALCVD was to control the precise growth of dielectric oxides for thin film electroluminescent (TFEL) display [Ritala, 1997]. Since then, a variety of materials have been deposited by ALCVD, including II-VI and III-V compound semiconductors, nitrides, oxides, fluorides, metal elements, and others. The films grown by ALCVD have been used in solar cells and also examined in the preparation of heterogeneous catalysts with a porous high surface area [Ritala, 1997; Haukka et al., 1997; Suntola, 1996]. Since ALCVD is based on the self-limiting surface reactions of reactants, a good conformativity of thin film over the substrate with a complex geometry is ensured, and therefore ALCVD is very suitable method for film deposition on porous materials.

One of the most important applications of ALCVD can be found in the nano-fabrication technology of electronic devices. As the design rule of miniaturizing microelectronics, the nano-thickness control of thin film is necessarily required to develop more dense integrated circuits [George et al., 1996; Leskela et al., 1995]. For example, in metal oxide semiconductor field effect transistor (MOS-FET) devices, as the channel length decreases, a required dielectric oxide thickness for the gate becomes sub nano-meter. International technology roadmap of semiconductor (ITRS) predicts that an equivalent oxide thickness will become below 0.8 nm in tera-bit memory chips. This ultra thin film consists of only a few atomic layers.

Conventional thin film growth techniques, such as chemical vapor deposition (CVD), physical vapor deposition (PVD) and plasma deposition method, have limitations on the control of nano-scale film growth. An atomic layer by layer growth is applicable only for ALCVD to this nano-deposition of thin films [Leskela et al., 1995; George et al., 1996].

ALCVD has also been employed to deposit conductor materials such as Cu, W, etc. [Chang et al., 1999; Klaus et al., 2000; Juppo et al., 1997; Solanki and Pathaney, 2000; Utriainen et al., 2000; Martensson and Carlsson, 1998], barrier materials (TiN, W<sub>x</sub>N, TaN, etc.) [Ritala et al., 1998; Kim et al., 2000; Klaus et al., 2000; Park et al., 2001] and capacitor dielectrics (Ta<sub>2</sub>O<sub>5</sub>, SBT, etc.) [Kukli et al., 1997; Vehkamaki et al., 1999].

Several unique advantages of ALCVD compared with other conventional deposition techniques make it a powerful deposition method in nano-fabrication. Those advantages are accurate control of film thickness, sharp interfaces, uniformity over large areas, excellent conformality over complex-shaped substrates, low temperature mildly oxidizing process, multilayer processing capability, and layer by layer control [Ritala et al., 1999; Ritala, 1997; Suntola, 1992; Leskela et al., 1995]. Potential applications of ALCVD under investigation are for the processing of hard mask, membranes, magnetic thin film head, flat panel display, photomask, inkjet printer and microelectromechanical system (MEMS) [Ritala et al., 1999; Ritala, 1997; Leskela et al., 1995].

#### 2. Characteristics of ALCVD

Due to the self-limiting reactions of chemical reactants on the substrate surface [George et al., 1996; Haukka et al., 1997; Suntola, 1996], ALCVD can grow the film with only one monolayer or sub-monolayer, which is chemisorbed in each reactant pulse-supply into the ALCVD reactor. Physisorbed multilayers over the layer chemisorbed on the substrate surface are removed during purge by inert gases and also can be easily removed by heating the substrate. In general, chemisorbed molecules have functional groups, which react with sequentially supplied gas molecules by exchange

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reactions (see Fig. 2) [George et al., 1996]. In a successive reactant pulse, a second self-limiting monolayer of molecules will be chemisorbed on the first atomic layer, and thus a layer by layer growth proceeds. Therefore, the desired film thickness can be produced simply by counting the number of reactant pulses. More details of ALCVD growth mode and mechanism will be presented in the next chapter.

Characteristics of ALCVD are summarized as follows [Ritala et al., 1999; Ritala, 1997; Suntola, 1992; Leskela et al., 1995].

#### Self-limiting growth process

- Film thickness depending only on the number of cycles
- Atomic level control of composition
- Large area uniformity and conformality
- Independence of reactant fluxes

#### Low temperature process

##### Separate dosing of reactants

- No gas phase reactions between reactant sources
- Freedom of choosing reactants

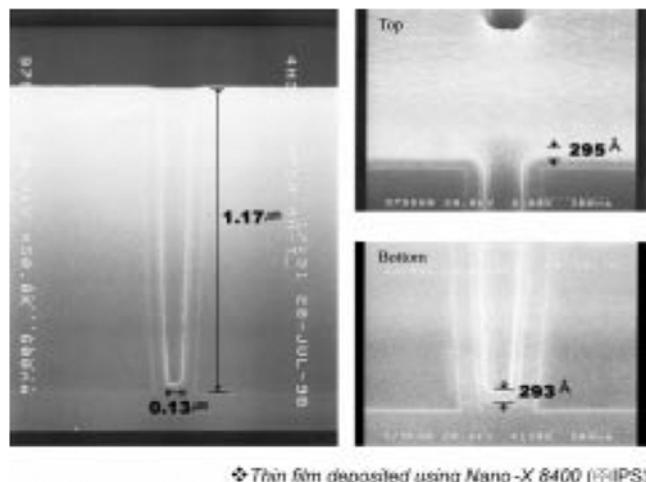
#### Wide temperature windows

- Capability to prepare multilayer structures

ALCVD can be considered as a modified chemical vapor deposition (CVD). Characteristics of those two processes are compared and listed in Table 1. Compared with a conventional CVD, ALCVD has many advantages, some of which are already mentioned above. However, one of disadvantages of ALCVD is slow process, which [Ritala, 1997] gives a low growth rate, resulting in a low throughput. The low throughput can be improved by developing a more efficient reactors and reactive precursors [Ritala, 1997].

ALCVD proceeds by cycles of reactant pulse steps and purge steps [Ritala et al., 1999; Suntola, 1994]. Number of pulses and time duration depends on the components of the film and the reactivity of precursors. For example, a binary oxide film needs a growth cycle of four pulses in general: a) the first pulse of a metal source  $\rightarrow$  b) purge  $\rightarrow$  c) the second pulse of an oxygen source  $\rightarrow$  d) purge. After one cycle, the film thickness is in general sub-monolayer. Time duration required for one cycle can be shortened by using more reactive precursors and more efficient reactors. Also, a large batch processing of ALCVD can make high productivity in the process for the deposition of high quality thin films onto large area substrate [Ritala, 1997].

One of the most important features of ALCVD is that this pro-



Thin film deposited using Nano-X 8400 (NIPS)

Fig. 1. A cross-section of thin film deposited on hollow trench by ALCVD, which shows an excellent conformality of film thickness.

cess ensures high conformality due to the controllability of adsorption. Fig. 1 shows an example of films deposited on a hollow via ALCVD with a high aspect ratio (depth/width) of 9. A uniform and continuous nano-scale film is observed, showing an excellent conformality. Therefore ALCVD can be used to deposit uniform, thin films on complex substrates like porous materials.

## PRINCIPLES OF ALCVD

### 1. Surface Reaction of ALCVD

Since ALCVD is based on a saturated, self-limiting surface reaction of precursor, a surface chemistry is important in order to understand the growth mechanism and optimize the ALCVD process [George et al., 1996; Haukka et al., 1997; Suntola, 1996]. The film growth rate, film structure, composition, and surface morphology are affected by the surface chemical reactions of precursors.

Main surface reactions involved in ALCVD are exchange reactions between functional groups of precursors [George et al., 1996]. For example,  $\text{MO}_2$  oxide thin films can be deposited through the following exchange reactions:

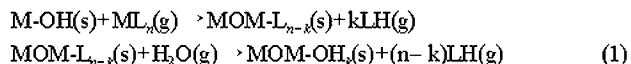


Table 1. Comparison between chemical vapor deposition (CVD) and atomic layer chemical vapor deposition (ALCVD)

	CVD	ALCVD
Reaction type	Surface reaction+gas phase reaction	Surface exchange reaction
Mode of adsorption and nucleation layer thickness	Chemisorbed and physisorbed agglomeration and growth with layer thickness greater than 20 Å	Chemisorbed monolayer nucleation layer thickness about a few Å
Deposition temperature	Relatively high	Relatively low (ALCVD window exists)
Step coverage	Good conformality	Good conformality
Thickness control	Difficult because of high growth rate	Easy because of low growth rate (<1 ML/cycle)
Composition control	Relatively difficult	Relatively easy control in atomic level
Throughput (growth rate)	High	Low (< a few hundreds nm/hr)

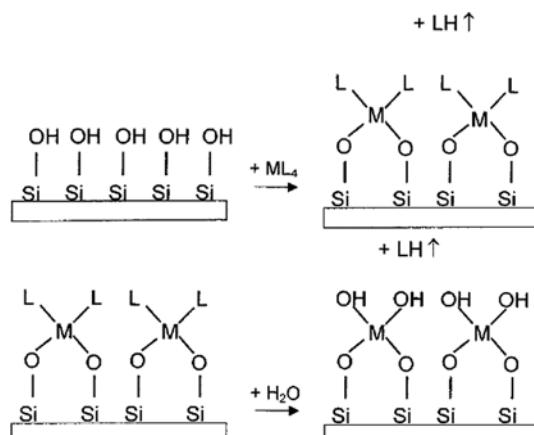


Fig. 2. Growth mechanism of metal oxide by ALCVD, showing exchange reactions between functional groups of precursors.

Where M and L are a metal and a ligand, respectively. Fig. 2 shows a schematic diagram of direct exchange reactions occurring during ALCVD of oxide thin films. A saturation of chemisorption takes place when the available surface bonding sites (OH) are all occupied by precursor ( $ML_n$ ) and the adsorbed species do not create new bonding sites for the dosed precursors [Haukka et al., 1997]. OH functional groups are replaced by new functional groups L. New functional group L does not act as bonding sites for  $ML_n$ . In the next saturated chemisorption, the surface is exposed to a different precursor ( $H_2O$ ) and new surface bonding sites (OH) are formed by exchange reactions between L and  $H_2O$  on the surface. A series of repetitions of these exchange reactions gives a layer by layer growth of metal oxide thin film.

The number of available bonding sites is important for the saturation of reaction sites [Haukka et al., 1997]. The saturation density strongly depends on the number and distribution of bonding sites of the surface. For example, the number of hydroxyl groups on silica depends on the preheat temperature of the surface. Hydroxyl groups act as a bonding site for the precursor chemisorption, and its density decreases as the surface temperature increases due to the dehydrogenation of OH. The saturation density of chemisorbed mole-

cules also depends on the molecular size of precursors. In ALCVD process, precursors chemisorbed on the surface retain functional groups. The density of atoms in a saturated monolayer is determined by packing density of the adsorbed precursor molecules [Haukka et al., 1997; Suntola, 1996]. Larger molecule gives a lower saturation density because of the steric hindrance effects. The lower saturation density results in lower growth rate. Another factor affecting saturation density is an adsorption configuration. Different types of adsorption (on-top, two-fold, three-fold, four-fold) on the surface will also change the saturation density and growth rate [Ylilammi, 1996].

A choice of precursors is critical in the process conditions and the film properties, including process window, growth rate, crystalline structure, residues in film, etc. Several requirements for proper precursors are listed as follows [Leskela et al., 1999]:

- High vapor pressure
- Thermal stability at substrate temperature
- Aggressive reactivity between different precursors
- No reaction with film and no etching of the film
- Production of volatile and unreactive by-products

In a CVD process, aggressive reactions between precursors should be prevented because they will induce gas phase reactions and yield undesirable by-products. However, in ALCVD, different kinds of precursors are introduced separately in a sequence cycle and thus gas phase reactions are eliminated. Active reactions between precursors dosed separately are required in ALCVD because it results in short pulse times, effective use of precursors, pure films, and low growth temperature [Leskela et al., 1999]. Table 2 shows growth characteristics using common ALCVD precursors, such as halides, alkoxides,  $\beta$ -diketonates, and water.

## 2. ALCVD Mode

Fig. 3 shows the process mode of ALCVD, processing by cycles of reactant pulse steps and purge steps between reactant pulses [Suntola, 1994; Ritala et al., 1999]. A pulse reactant vapor is dosed onto a substrate in an ALCVD reactor and a self-limiting chemisorbed monolayer of reactant is formed. After excessive exposure of gas phase reactants and purging by-products by inert gas from the reac-

Table 2. ALCVD growth characteristics of common precursors including halides, alkoxides,  $\beta$ -diketonates, and water

Precursor	Advantages	Disadvantages
Halide ( $MCl_n$ )	Volatile, Very reactive High thermally stability ⇒ wide ALCVD window	Highly corrosive Producing reactive by-product (HCl) ⇒ readsorption, rough surface Chlorine residues at low $T_s$
Alkoxide $M(OR)_n$	Good self-limiting characteristics at low growth temperature ( $T_s$ ) Good films properties at high $T_s$ (high refractive index, no carbon residue)	Thermal decomposition at high $T_s$ (CVD type deposition) Carbon residue at low $T_s$ Phase transition at low $T_s$ ⇒ surface roughness increases
$\beta$ -diketonates	Alkaline earth and rare earth metal precursors	Needs high reactive oxygen source, like ozone Low vapor pressure
Water ( $H_2O$ )	Formation of hydroxyl groups ⇒ Active sites for chemisorption Growth rate $\propto$ density of OH-groups	Low reactivity at low $T_s$ ⇒ addition of $O_3$ or $H_2O_2$ Dehydroxylation at high $T_s$

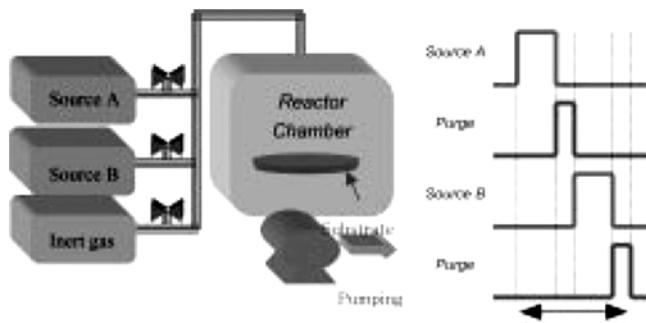


Fig. 3. Schematic diagram of ALCVD reactor system and growth cycle. A cycle consists of reactant pulse steps and purge steps between reactant pulses.

tor, then another reactant source is pulsed into the reactor. Chemical exchange reactions proceed between adsorbed layer and dosed precursors, and another chemisorbed monolayer is formed [George et al., 1996]. Again gas phase species are purged from the reactor by the next purge. The number of steps in a cycle depends on the components of the films. In general, there are two ALCVD reactor types: MBE-type and CVD-type [Suntola, 1994]. In MBE type, a

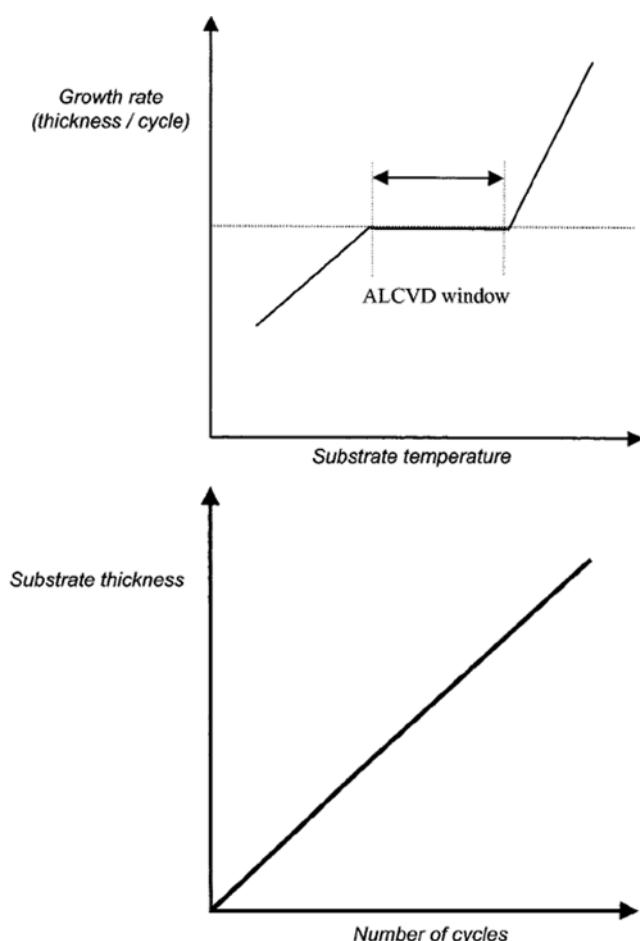


Fig. 4. Schematic diagram of ALCVD growth temperature window. Within ALCVD window, the growth rate does not depend on the growth temperature and only depend on the number of cycles.

reactor pressure is in ultra-high vacuum condition and reactants are introduced by using Knudsen cells. Dose duration is determined by controlling a shutter in front of the cell. In CVD-type reactors, a reactor pressure is in low vacuum ( $>1$  torr). It uses a modified CVD reactor with a cyclic dosing system. To improve reactor efficiency, flow type reactor with small radius can be used as a multi-shot reactor [Suntola, 1994].

Several reaction conditions are required for a saturated, self-limiting chemisorption of precursors [Haukka et al., 1997; Suntola, 1996]. The required conditions are adequate surface temperature for an activated chemisorption of precursor, thermal stability of the precursor to avoid thermal decomposition, sufficient dosing amount of precursor for saturated adsorption, and availability of bonding sites. Dependence of growth rate on the substrate temperature is shown in Fig. 4. Within ALCVD window, the growth rate does not depend on the substrate temperature and it only depends on the number of cycles. The film thickness varies linearly with the number of cycles, and thus the film thickness is easy to control [Suntola, 1994]. At temperatures lower than ALCVD window, the growth rate decreases because the thermal energy of the substrate is insufficient for activated chemisorption of the precursors. At temperatures higher than ALCVD window, growth rate rapidly increases because precursors are thermally decomposed and nucleation rate becomes much higher than monolayer formation. ALCVD window depends on the substrate and precursors. For saturated surface reactions of precursors on the substrate, a sufficient amount of precursor should be dosed into the reactor. Once the dose amount is more than a critical value for saturated chemisorption, then the growth rate is independent of the reactant fluxes [Haukka et al., 1997; Suntola, 1996].

### 3. Diagnostics of ALCVD

To understand the basic mechanism of ALCVD growth and optimize the process, *in-situ* growth monitoring and basic surface chemistry are important [Yamamoto et al., 2001; George et al., 1996]. Since, in general, ALCVD proceeds in flow reactor systems, the pressure is too high for using *in-situ* electron or ion spectroscopy. Instead, optical probing methods can be used for *in-situ* analysis. *In-situ* optical monitoring methods such as surface photo-absorption (SPA), ellipsometry and reflectance difference spectroscopy (RDS) have been employed for the analysis of ALCVD growth [Yamamoto et al., 2001; Klaus et al., 1997]. SPA has been used to have real-time information on GaAs epitaxial growth reactions on the substrate surface during ALCVD [Koukitu et al., 1996]. Also chemisorption of molecules on the surface during ALCVD has been studied by using SPA. RDS is another *in-situ* growth monitoring method in semiconductor industry by means of optical probing. The growth rate and roughness of metal oxide thin films are detected by using optical diagnoses. RDS also gives information about segregation during hetero-epitaxial growth by ALCVD [Ares et al., 1995].

Real-time quartz crystal microbalance (QCM) has been used to study the deposition kinetics of ALCVD process [Aarik et al., 2001; Kukli et al., 2000]. The mass changes during ALCVD cycles were measured and analyzed to investigate the kinetics of precursor adsorption. Thermal decomposition of precursors and self-limiting feature of adsorption are studied by QCM. Surface reaction mechanism has been proposed for ALCVD growth of various oxide films using QCM analysis. Mass spectrometry has been used as another

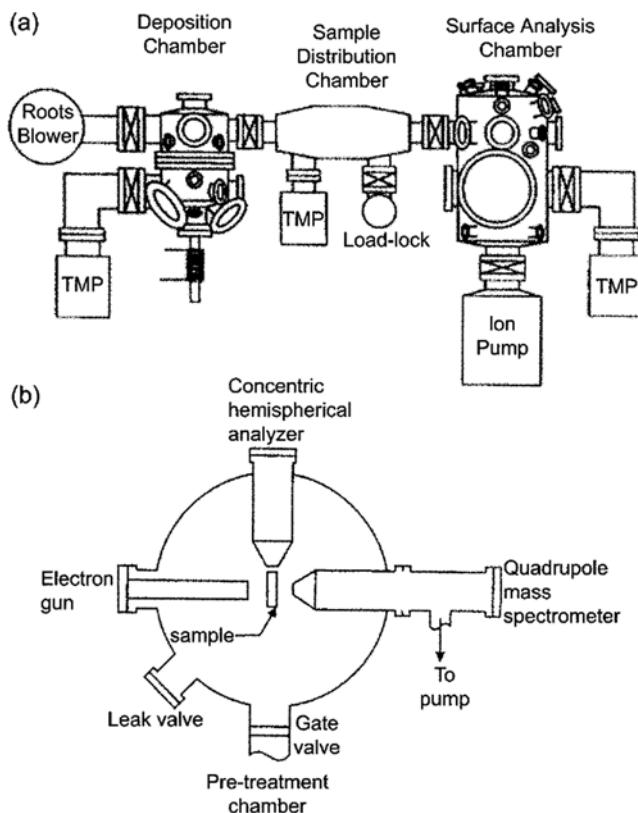


Fig. 5. (a) Deposition, sample delivery, and surface analysis chambers [Kellerman et al., 1995]. (b) Schematic view of analysis chamber [Cho et al., 2001].

*in-situ* monitoring method of ALCVD growth [Juppo et al., 2000; Rahtu et al., 2001; Ritala et al., 1999]. Mass spectrometry can be used to analyze volatile decomposition products of surface reaction during ALCVD. This analysis can give information about the precursor decomposition and the growth mechanism of ALCVD. Using mass spectrometry in ALCVD system requires a gas sampling chamber with differential pumping because the operating pressure of a mass-spectrometer is much lower than the pressure of ALCVD process.

Since ALCVD is based on self-limiting surface reaction of precursors, a study of surface reaction is important in order to understand the growth mechanism. However, direct surface reaction studies of ALCVD are difficult in many cases because most surface chemistry techniques require UHV (ultra-high-vacuum) environments. If a growth system is connected with an analysis system through a proper transfer system as shown in Fig. 5 [Kellerman et al., 1995], then the surface reaction mechanism of the ALCVD process can be analyzed by transferring a sample from the growth chamber to the characterizations chamber. Auger electron spectroscopy (AES), Fourier transformed infrared spectroscopy (FTIR), temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectroscopy (SIMS) have been applied to study the self-limiting saturated surface chemisorption of precursors and direct surface exchange reactions of functional groups occurring during ALCVD process [George et al., 1996; Luo et al., 1998; Kuo et al., 2000]. Among these techniques, FT-IR is one of the most widely used techniques. Fig. 6 shows typical sur-

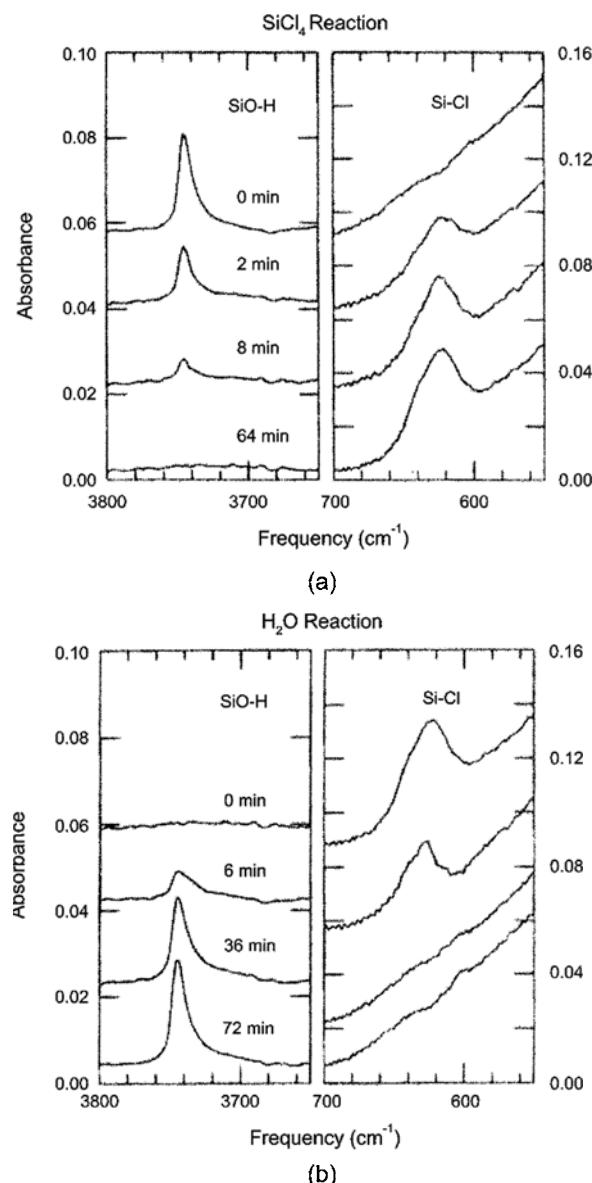


Fig. 6. FT-IR spectra of Si-Cl and SiO-H stretching vibration during (a) SiCl<sub>4</sub> and (b) H<sub>2</sub>O pulse [George et al., 1996].

face exchange reactions for ALCVD growth of SiO<sub>2</sub> using SiCl<sub>4</sub> and H<sub>2</sub>O [George et al., 1996]. Direct exchange reactions between functional groups, Cl and OH, were studied by monitoring the adsorption peak intensity changes corresponding to Cl and OH bond during SiCl<sub>4</sub> and H<sub>2</sub>O exposures. Similar studies were performed for Al<sub>2</sub>O<sub>3</sub> ALCVD [George et al., 1996]. In addition to FT-IR, other techniques including AES, TPD, XPS, and SIMS have been used to understand ALCVD growth mechanism of various materials. Some examples of surface chemistry studies for ALCVD are summarized in Table 3. Those studies give information about optimizing ALCVD process conditions, precursor screening, impurity incorporation in films, film crystallinity, morphology, and growth kinetics.

## APPLICATIONS OF ALCVD

ALCVD can be applied in various areas, such as microelectron-

**Table 3. Some examples of surface chemistry techniques for ALCVD**

Deposited materials	Surface chemistry techniques	Obtained Information from surface analysis	References
SiO <sub>2</sub>	FT-IR	-Surface exchange reactions	[George et al., 1996]
TiO <sub>2</sub>	In-Situ Mass Spectrometry	-Surface exchange reactions -Reaction products	[Rahtu et al., 2001]
HfO <sub>2</sub>	QCM	-Surface exchange reactions -Self-limiting growth condition	[Aarik et al., 1999]
W	AES	-Layer by layer growth mode -Contaminations of films	[Elam et al., 2001]
AlN	SIMS	-Surface exchange reactions	[Kuo and Rogers, 2000]
AlN	TPD	-Desorption pathway	[Kuo and Rogers, 2000]
Al <sub>2</sub> O <sub>3</sub>	XPS	-Chemical bonding state -Contaminations of films	[Yang et al., 2000]

ics, optoelectronics, catalysis, membrane, and display. Among these applications, this article concentrates on the microelectronic applications, where a nano-scale thin film growth becomes crucial in near future device fabrications.

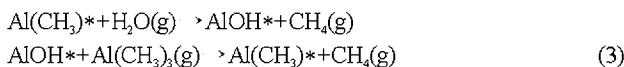
### 1. Gate Dielectrics

SiO<sub>2</sub> has been used as a conventional gate oxide of MOS (metal oxide semiconductor) devices. On miniaturizing the size of devices, the equivalent oxide thickness is decreased and tunneling leakage current and dielectric breakdown will give undesirable properties to devices. For this reason, other gate oxide materials with high dielectric constant are required to replace SiO<sub>2</sub>. An equivalent oxide thickness of the gate material can be shown as the following equation [Ritala et al., 2000].

$$t_{eq} = \frac{3.9}{\epsilon} t_{oxide} \quad (2)$$

Where  $t_{eq}$ ,  $t_{oxide}$  are equivalent oxide thickness and SiO<sub>2</sub> thickness, respectively, and  $\epsilon$  is a dielectric constant of a material. Equivalent oxide thickness means the thickness of the oxide, which has the same capacitance as that of SiO<sub>2</sub> with the same thickness.

Al<sub>2</sub>O<sub>3</sub> is one of the widely studied oxide materials by ALCVD. Al<sub>2</sub>O<sub>3</sub> has a medium permittivity (about 10) and is one of candidates for replacing SiO<sub>2</sub>, a conventionally used gate dielectric, for a future MOS device. Al<sub>2</sub>O<sub>3</sub> has suitable properties as a gate dielectric material such as high thermal stability, low leakage current and good interfacial property with Si [Ericsson et al., 1997; Kim et al., 1997; Yang et al., 2000; Park et al., 2001]. Al<sub>2</sub>O<sub>3</sub> has also a low permeability of alkali ions and other impurities. Thus it can be used as an attractive ion barrier material in TFEL (thin film electro-luminescent) display devices [Tiitta et al., 1998]. For ALCVD process of Al<sub>2</sub>O<sub>3</sub>, AlCl<sub>3</sub> has been widely used as a metal source. In the case of using AlCl<sub>3</sub>, growth temperature is relatively high (about 500 °C) and grown films have chlorine impurities [Ritala et al., 1996]. Non-chlorine precursors have been also used for Al<sub>2</sub>O<sub>3</sub> ALCVD. TMA [trimethylaluminum=Al(CH<sub>3</sub>)<sub>3</sub>] is a widely used non-chlorine precursor. The growth mechanism of Al<sub>2</sub>O<sub>3</sub> ALCVD using TMA and water is proposed as follows [Yun et al., 1997].

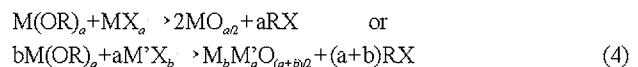


The ALCVD window of the process is 150–400 °C. It is known that current leakage and contaminations of carbon and hydrogen in the

film decreased with increasing growth temperature. Growth rate decreased at high temperatures because a dehydroxylation reaction occurs on hydroxylated surfaces at high temperatures [Juppo et al., 2000]. Although there was no chlorine residue in films grown by using TMA, there were still C, H contaminations found in grown films. Beside TMA and AlCl<sub>3</sub>, other precursors, such as Al(CH<sub>3</sub>)<sub>2</sub>Cl [Kukli et al., 1997], DMEAA(AIH<sub>3</sub> : N(CH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)) [Jeong et al., 2001], Al(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> [Niimisto et al., 1996] have been used as a metal source. The growth characteristics using those precursors are summarized in Table 4.

To lower growth temperature, modified ALCVD processes like PE-ALCVD (Plasma enhanced ALCVD), have been tried. When Al<sub>2</sub>O<sub>3</sub> film is grown by PE-ALCVD using DMEAA and H<sub>2</sub>, growth temperature is in the range of 100–125 °C, which is much lower than non-plasma ALCVD [Jeong et al., 2001].

Recently, other high  $k$  (dielectric constant) materials such as ZrO<sub>2</sub> [Na et al., 2002; Perkins et al., 2001; Kytokivi et al., 1997; Kukli et al., 2000], HfO<sub>2</sub> [Aarik et al., 1999; Ritala and Leskela, 1994; Aarik et al., 2001], La<sub>2</sub>O<sub>3</sub>, [Nieminen et al., 2001], Y<sub>2</sub>O<sub>3</sub> [Puitkonen et al., 2001], Zr-silicate [Ritala et al., 2000], and Hf-silicate [Gordon et al., 2001] have been studied for applications as future CMOS gate dielectrics. ZrO<sub>2</sub> and HfO<sub>2</sub> have high permittivity (20–30) and good chemical stability. For ALCVD process of these oxides, halide precursors, such as HfCl<sub>4</sub> and ZrCl<sub>4</sub>, have been mostly used. In those cases, the structure of grown films is amorphous. When growth temperature was increased, the crystallinity of the films improved concurrently with the decrease of chlorine contaminations. However, the growth temperature was still high (about 500 °C) and undesirable silicate layers were formed in a grown oxide-silicon substrate interface. These interface silicates decrease an equivalent oxide thickness because silicates have lower dielectric constants than high- $k$  single oxides. The formation of native oxides and silicates at the interface is unavoidable when water, O<sub>2</sub> and O<sub>3</sub> are used as an oxygen source for an oxide ALCVD. To solve these problems, a metal alkoxide (M-OR) has been proposed as an oxygen source [Ritala et al., 2000]. For an alkoxide metal, thin films can be grown by the following mechanism,



If Si used instead of metal in the above reaction, then silicate materials can be grown. Recently, ALCVD growth of Hf-silicate and Zr-

**Table 4. Applications of atomic layer chemical vapor deposition for various materials**

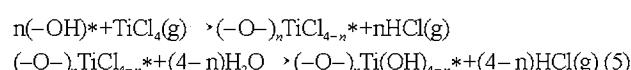
Materials	Precursors	Growth temperature (°C)
<i>Gate dielectric</i>		
Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub> +H <sub>2</sub> O/glass Al(CH <sub>3</sub> ) <sub>3</sub> +H <sub>2</sub> O/Si(100) Al(CH <sub>3</sub> ) <sub>3</sub> +H <sub>2</sub> O/SiO <sub>2</sub> /Si Al(CH <sub>3</sub> ) <sub>2</sub> Cl+H <sub>2</sub> O/glass AlH <sub>3</sub> : N(CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )+H <sub>2</sub> /Si AlCl <sub>3</sub> +Al(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> /Si AlCl <sub>3</sub> +Al(OC <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> /Si Al(CH <sub>3</sub> ) <sub>3</sub> +Al(OC <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> /Si Al(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> +H <sub>2</sub> O or ROH or O <sub>2</sub> Al(OC <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> +H <sub>2</sub> O or ROH or O <sub>2</sub>	500 250-400 350, 370 180-250 100-125 400 300 300 250-500 250-500
ZrO <sub>2</sub>	ZrCl <sub>4</sub> +H <sub>2</sub> O/Si Zr(OC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> +H <sub>2</sub> O	300 150-300
HfO <sub>2</sub>	HfCl <sub>4</sub> +H <sub>2</sub> O/glass	500
La <sub>2</sub> O <sub>3</sub>	La(thd) <sub>3</sub> +ozone	225-275
Y <sub>2</sub> O <sub>3</sub>	Y(thd) <sub>3</sub> +ozone	200-425
Zr-silicate	ZrCl <sub>4</sub> +Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ZrCl <sub>4</sub> +Si(OC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>	500 250-500
Hf-silicate	Hf(N(CH <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> +(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> SiOH/Si	250-350
<i>Capacitor dielectric</i>		
TiO <sub>2</sub>	TiCl <sub>4</sub> +H <sub>2</sub> O/Si(111) TiI <sub>4</sub> +H <sub>2</sub> O/Si(100) Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> +H <sub>2</sub> O Ti(OC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> +H <sub>2</sub> O	100-300 230-375 100-300 150-350
Ta <sub>2</sub> O <sub>5</sub>	TaCl <sub>5</sub> +H <sub>2</sub> O Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +H <sub>2</sub> O/glass Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +TaCl <sub>5</sub>	80-500 225-325 275-325
LaMnO <sub>3</sub>	La(thd) <sub>3</sub> +Mn(thd) <sub>3</sub> +O <sub>3</sub> /glass or Si(100)	250-300
LaNiO <sub>3</sub>	La(thd) <sub>3</sub> +Ni(thd) <sub>3</sub> +O <sub>3</sub> /glass	215-250
SrTiO <sub>3</sub>	Sr(C <sub>5</sub> -i-pr <sub>3</sub> H <sub>2</sub> ) <sub>2</sub> +Ti(O-ipr) <sub>4</sub> +H <sub>2</sub> O/glass	325
BaTiO <sub>3</sub>	Ba(C <sub>5</sub> Me) <sub>2</sub> +Ti(O-ipr) <sub>4</sub> +H <sub>2</sub> O	275
<i>Copper, Diffusion barrier</i>		
Cu	CuCl+H <sub>2</sub> /Cu(100) CuCl+Zn/Al <sub>2</sub> O <sub>3</sub> Cu(tmhd) <sub>2</sub> +H <sub>2</sub> Cu(acac) <sub>2</sub> +H <sub>2</sub> /Si, glass Cu(hfac) <sub>2</sub> ·XH <sub>2</sub> O+methanol or ethanol or formalin	440-500 150-300 250 320
TiN	TiCl <sub>4</sub> +NH <sub>3</sub> /Si TiI <sub>4</sub> +NH <sub>3</sub> /glass TEMAT+NH <sub>3</sub> /Si TDMAT+NH <sub>3</sub> /Si	350-450 350-500 150-220 180
Ti-Si-N	TDMAT+SiH <sub>4</sub> +NH <sub>3</sub>	180
TaN	TBTDET+H <sub>2</sub>	260
W <sub>2</sub> N	WF <sub>6</sub> +NH <sub>3</sub> /Si	327-527

silicate has attracted attention as high-k material because they have good interfacial properties with Si substrate and high dielectric constants. Recent ALCVD results of various gate oxides are summarized in Table 4.

## 2. Capacitor Dielectrics

TiO<sub>2</sub> has good properties as a capacitor dielectric, such as high chemical resistance and high permittivity [Kim et al., 1998; Schuisky et al., 2000]. ALCVD growth of TiO<sub>2</sub> has been studied by using various precursors, such as TiCl<sub>4</sub> [Aarik et al., 1995, 1996, 1997;

Suisalu et al., 1998; Tarre et al., 2001], TiI<sub>4</sub> [Kukli et al., 2000] and Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> [Rahtu et al., 2001]. TiCl<sub>4</sub> is one of the most frequently used precursors. ALCVD growth mechanism of TiO<sub>2</sub> using TiCl<sub>4</sub> and H<sub>2</sub>O is proposed as follows.



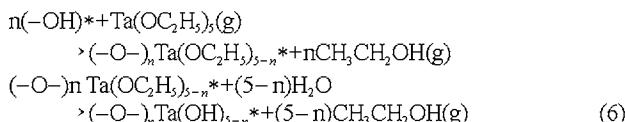
ALCVD films grown by using TiCl<sub>4</sub> have chlorine contamination and a by-product, HCl, which is corrosive and toxic. In addition to

**Table 4. Continued**

Materials	Precursors	Growth temperature (°C)
<i>Nano-laminates</i>		
HfO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +HfCl <sub>4</sub> +H <sub>2</sub> O/glass	325
	Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +HfCl <sub>4</sub> +H <sub>2</sub> O/Si	300
Ta <sub>2</sub> O <sub>5</sub> -Nb <sub>2</sub> O <sub>5</sub>	TaCl <sub>5</sub> +Nb(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +H <sub>2</sub> O/glass	325
	Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +Nb(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +H <sub>2</sub> O/glass	300-325
HfO <sub>2</sub> -ZrO <sub>2</sub>	HfCl <sub>4</sub> +ZrCl <sub>4</sub> +H <sub>2</sub> O/Si	300
Ta <sub>2</sub> O <sub>5</sub> -ZrO <sub>2</sub>	Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +ZrCl <sub>4</sub> +H <sub>2</sub> O/Si	300
Nb <sub>2</sub> O <sub>5</sub> -Al <sub>2</sub> O <sub>3</sub>	Nb(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +AlCl <sub>3</sub> +H <sub>2</sub> O/glass	300
Ta <sub>2</sub> O <sub>5</sub> -Al <sub>2</sub> O <sub>3</sub>	TaCl <sub>5</sub> +AlCl <sub>3</sub> +H <sub>2</sub> O/glass	300
(Nb <sub>1-x</sub> Ta <sub>x</sub> ) <sub>2</sub> O <sub>5</sub> -ZrO <sub>2</sub>	Ta(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +ZrCl <sub>4</sub> +Nb(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +H <sub>2</sub> O/glass	230-325
<i>Other Oxides</i>		
Nb <sub>2</sub> O <sub>5</sub>	Nb(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub> +H <sub>2</sub> O	230-260
In <sub>2</sub> O <sub>3</sub>	InCl <sub>3</sub> +H <sub>2</sub> O	500
SnO <sub>2</sub>	SnCl <sub>4</sub> +H <sub>2</sub> O	180-300
ITO	InCl <sub>3</sub> +SnCl <sub>4</sub> +H <sub>2</sub> O	500
ZnO	Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> +H <sub>2</sub> O	105-180
	ZnCl <sub>2</sub> +O <sub>2</sub>	450-550
MgO	Mg <sub>2</sub> (thd) <sub>4</sub> +H <sub>2</sub> O <sub>2</sub>	325-425
	Mg(thd) <sub>2</sub> +O <sub>3</sub>	225-250
	Mg(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> +H <sub>2</sub> O	200-300

TiCl<sub>4</sub>, other precursors such as TiI<sub>4</sub>, Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> have been used [Ritala et al., 1994]. TiO<sub>2</sub> ALCVD studies have indicated that the growth conditions and grown film properties are strongly affected by Ti-precursors. TiCl<sub>4</sub> shows a high thermal stability over a wide temperature range, ensuring a wide ALCVD window. In case of alkoxide precursors, thermal decomposition of precursors is observed at temperatures above 350 °C, which indicates a lower thermal stability of metal-alkoxides than that of metal-halides. Also, the crystallinity of TiO<sub>2</sub> film depends on precursors used. Polycrystalline TiO<sub>2</sub> films are obtained by using Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, while an amorphous film is obtained by using TiCl<sub>4</sub>. In TiO<sub>2</sub> ALCVD using TiCl<sub>4</sub> and H<sub>2</sub>O, the roughness of the film surface is increased with increasing growth temperature, while contaminations are decreased at high temperatures. The crystalline structure of the film also improved with growth temperature. Anatase structure is dominant at low temperatures but rutile and TiO<sub>2</sub>-II structures become dominant at high growth temperatures [Aarik et al., 1995, 1997; Suisalu et al., 1998].

Ta<sub>2</sub>O<sub>5</sub> is another widely studied material by ALCVD. Ta<sub>2</sub>O<sub>5</sub> has high chemical and thermal stability with a dielectric constant of 22-35 [Yun et al., 1997; Kukli et al., 1995]. TaCl<sub>5</sub> [Aarik et al., 1996; Kukli et al., 1995] has been used as a metal source. Ta<sub>2</sub>O<sub>5</sub> films using TaCl<sub>5</sub> also showed Cl contamination and produced corrosive HCl by-products. For the same reasons as that from TiO<sub>2</sub>, other precursors like Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> have been also used. When Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> and H<sub>2</sub>O were used, the films were grown by ALCVD at 250 °C by the following mechanisms [Kukli et al., 1997].



It is known that C and H contaminations decrease and growth rate

also decreases as growth temperature increase, due to the dehydroxylation reaction on hydroxylated surface [Kukli et al., 1997]. As mentioned above, the formation of native oxides and silicates in the interface is unavoidable when water, O<sub>2</sub> and O<sub>3</sub> are used as oxygen sources for oxide ALCVD. Recently, in order to decrease interface native oxides and contamination of impurities, several studies have been done. The reaction of alkoxide metal (M-OR) along with metal halide is an example of those studies [Kukli et al., 2000].

In general, simple single oxides such as TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, show high leakage current. Recently, ALCVD of high-k binary or ternary materials has attracted much attention because these oxide materials show a lower leakage current than that of single oxides [Vehkamaki et al., 1999] and also can be used as ferroelectrics due to their perovskite structures [Chung and Kim, 1997; Kim and Kwon, 1999; Seim et al., 1997]. The composition of binary oxides can be easily controlled by adjusting relative pulse lengths of precursors [Nilsen et al., 1999]. Examples of ALCVD growth of binary oxides are LaMnO<sub>3</sub>, [Nilsen et al., 1999], LaNiO<sub>3</sub>, [Seim et al., 1997], SrTiO<sub>3</sub> and BaTiO<sub>3</sub>, [Vehkamaki et al., 1999]. These films are obtained with the deposition of each single oxide followed by post-annealing at 500-650 °C, which makes binary oxides by reacting as-deposited single oxides. These requirements of post-annealing to obtain binary oxides are currently the main limitations of ALCVD [Vehkamaki et al., 1999]. ALCVD of capacitor dielectrics is also summarized in Table 4.

### 3. Nano-Laminates

A nano-laminate is a structure that has repeated bilayer stacks. This structure must have high permittivity, high breakdown resistance, good stability and high chemical inertness [Kukli et al., 1996]. Even though nano-laminates are composed of the same kind of bilayer materials, the properties strongly depend on the growth temperature and the relative thickness ratio of repeated bilayer stacks [Kukli et al., 1997]. ALCVD has many advantages for making this structure because films grown by ALCVD have good uniformity

and the thickness of each film can be easily controlled by ALCVD. Various nano-laminates have been grown by ALCVD, including  $\text{HfO}_2\text{-Ta}_2\text{O}_5$  [Zhang et al., 2000; Zhang and Solanki, 2001],  $\text{Ta}_2\text{O}_5\text{-Nb}_2\text{O}_5$  [Kukli et al., 1999, 2001],  $\text{HfO}_2\text{-ZrO}_2$  [Zhang et al., 2000; Zhang and Solanki, 2001],  $\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3$  [Kukli et al., 2001],  $\text{Ta}_2\text{O}_5\text{-Al}_2\text{O}_3$  [Katrelius et al., 1993] and  $(\text{Nb}_{1-x}\text{Ta}_x)_2\text{O}_5\text{-ZrO}_2$  [Kukli et al., 1997]. An  $\text{HfO}_2\text{-Ta}_2\text{O}_5$  nano-laminate is one of the most studied structures.  $\text{HfCl}_4$  and  $\text{Ta}(\text{OC}_2\text{H}_5)_5$  or  $\text{TaCl}_5$  are used as the source of Hf, Ta sources, respectively.  $\text{H}_2\text{O}$  is used as an oxygen source to grow  $\text{HfO}_2\text{-Ta}_2\text{O}_5$  nano-laminates at 300-330 °C. The resulting nano-laminate has better uniformity and higher permittivity than that from single oxides of the same thickness. Especially, leakage current considerably decreased due to the formation of amorphous  $\text{Ta}_2\text{O}_5$  interrupting growth of grain boundaries [Kukli et al., 1996]. Grain boundaries within films are considered as main paths of current leakage. Various nano-laminate structures grown by ALCVD are summarized in Table 4.

#### 4. Copper Metallization and Diffusion Barriers

Copper has been grown mostly by electroplating for interconnect applications. Electrodeposited Cu layers need very thin Cu seed layers with good uniformity for better adhesion to the substrate. ALCVD has attracted attention for depositing these Cu seed layers [Solanki and Pathangay, 2000]. ALCVD of Cu seed layers is a single element film deposition process. Therefore, reducing agents, such as  $\text{H}_2$  and Zn, are required to remove functional groups of precursors through surface reactions and also provide chemisorption sites for Cu precursors [Chang et al., 1999; Klaus et al., 2000; Juppo et al., 1997; Martensson et al., 1998]. Cu thin films can be obtained by ALCVD through the reactions in Eq. (7) [Utriainen et al., 2000].



where L indicates an organic or inorganic ligand. One of the simple Cu precursors is  $\text{CuCl}$ . When  $\text{CuCl}$  is used for the ALCVD process, it is known that growth temperature is relatively high (about 400-500 °C). For decreasing growth temperature,  $\beta$ -diketonate precursors, such as  $\text{Cu}(\text{acac})_2$  and  $\text{Cu}(\text{hfac})_2\text{-XH}_2\text{O}$ , have been studied [Solanki, and Pathangay, 2000; Utriainen et al., 2000; Martensson and Carlsson, 1998]. For  $\text{Cu}(\text{hfac})_2\text{-XH}_2\text{O}$  and methanol, ethanol or formalin, the growth temperature is decreased to 150-300 °C.

In copper interconnects, a diffusion barrier must be required because copper is easy to diffuse into a silicon well [Utriainen et al., 2000; Kim et al., 2000]. A very thin diffusion barrier must have low resistivity and dense microstructures. Also, diffusion barriers should not react with copper and these thin films must be deposited at low temperatures (below 400 °C) [Juppo et al., 2000]. TiN has been grown by ALCVD by using various titanium sources, such as  $\text{TiL}_4$  [Ritala et al., 1998],  $\text{TiCl}_4$  [Jeon et al., 2000], TEMAT( $\text{Ti}(\text{NC}_2\text{H}_5\text{CH}_3)_4$ ) [Kim et al., 2000; Min et al., 1998] and TDMAT( $\text{Ti}(\text{NCH}_3\text{CH}_3)_4$ ) [Lim et al., 2001], with  $\text{NH}_3$  as a nitrogen source. When halide precursors are used, films are grown at 350-500 °C. Contamination and resistivity of films are decreased with high growth temperature. When the growth temperature is relatively high, chlorine contamination increases the resistivity of the films. Other precursors, such as TDMAT and TEMAT, have been tried instead of halide precursors [Yun et al., 1999]. When the films were grown by using these precursors, growth temperature was 150-220 °C and chlorine residue could be avoided [Kim et al., 2000; Min et al., 1998; Lim et al., 2001].

Ti-Si-N [Min et al., 2000],  $\text{TaN}$  [Park et al., 2001] and  $\text{W}_2\text{N}$  [Klaus et al., 2000] also have good properties as diffusion barriers. Especially, Ti-Si-N films have been deposited to improve interfacial properties with silicon. However, these diffusion barrier materials grown by ALCVD in general show too low growth rates, high resistivity and also aging effects [Kim et al., 2000; Park et al., 2001]. ALCVD growth of Cu and various diffusion barriers are summarized in Table 4.

#### 5. Other Oxides

Beside the oxide, nitride and metal thin films mentioned above, other various oxides have been grown by ALCVD for microelectronic applications. These oxides include  $\text{Nb}_2\text{O}_5$  [Kukli et al., 1998],  $\text{In}_2\text{O}_3$  [Asikainen et al., 1997],  $\text{SnO}_2$  [Asikainen et al., 1994], ITO ( $\text{In}_2\text{O}_3\text{:Sn}$ ) [Asikainen et al., 1996],  $\text{ZnO}$  [Canava et al., 2000; Yousfi et al., 2000; Yamada et al., 1997; Sang et al., 1998; Kaiya et al., 2001] and  $\text{MgO}$  [Hatanpaa et al., 1999; Putkonen et al., 2000]. These results are also summarized in Table 4.

## CONCLUSIONS

As a nano-processing tool, ALCVD has good characteristics for depositing atomic layer thin films. ALCVD is based on the self-limiting chemisorption of precursors, which enables the digital control of film thickness in atomic-scale, uniformity over large area, easy control of film compositions, low growth temperature, and wide process window. ALCVD has been used to deposit various materials, including oxides, nitrides, metals, semiconductors, etc. Selection of chemical precursors, growth temperature, precursor dosing amount and cycle time is critical for a successful ALCVD growth of thin films. Optimum growth conditions depend on the reactivity of precursors, substrate materials and reactor design. A better understanding of surface chemistry involved in ALCVD is important to figure out the growth mechanism and the optimization of ALCVD process. Various methods to diagnose ALCVD process have been studied, but much more effort is required in order to understand the film deposition mechanism. In conclusion, ALCVD is a very suitable method for the construction of atomic-scale thin films that will play an important role in the future nano-fabrication.

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