Atomic Layer Deposition for Continuous Roll-to-Roll Processing

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ABSTRACT

Atomic layer deposition (ALD) is currently being developed for continuous roll-to-roll processing. This development is significant because roll-to-roll processing would allow ALD to address many applications in a cost effective manner. This paper overviews the approaches and progress to date. The original idea of ALD with moving substrates and constant precursor flows was presented in a patent by Suntola and Antson in 1977. This scheme involved rotating the substrate between alternating precursor sources and vacuum pumping regions. One current approach under development is based on moving the substrate close to a gas source head. The ALD precursors continuously flow through slits in the gas source head that are separated and isolated by inert gas purging. A second version of this design involves using a gas bearing to set the gap spacing between the gas source head and substrate. Another ongoing approach is based on moving the substrate through separate regions of precursor pressure and inert gas purging. Limited conductance between the regions prevents the gas phase reaction of the ALD precursors. The paper examines the issues and prospects for achieving ALD for continuous roll-to-roll processing. Additional details are presented for the dependence of precursor isolation on reactor parameters for a substrate under a model gas source head.

INTRODUCTION

Atomic Layer Deposition (ALD) is a thin film growth technique based on sequential, self-limiting surface reactions [1, 2]. ALD is capable of atomic level control of thin film growth. ALD can also deposit very conformally on high aspect ratio substrates [3]. Many materials can be deposited using ALD [4]. ALD is currently being commercialized by the semiconductor industry and is used to form gate oxides for field effect transistors and capacitors for dynamic random access memory devices.

ALD is performed in various types of reactors including low pressure reactors operating in viscous flow [5] and higher vacuum reactors that enable plasma processing [6]. ALD has also been performed at atmospheric pressure [7, 8]. In most of the previous implementations of ALD, the reactants are pulsed into the reactor and then removed by purging or vacuum pumping. A schematic of this time sequence for Al2O3 ALD using trimethylaluminum (TMA) and H2O is shown in Figure 1. The substrates remain fixed in one location in the reactor. The previous reactant must be completely removed from the reactor to avoid gas phase reactions that would lead to chemical vapor deposition (CVD). The reactants are separated from each other in time to prevent CVD. This process is repeated in an ABAB... sequence to grow the ALD film.

Alternative ALD approaches also are possible that separate the reactants in space rather than in time. In this version of ALD, the two reactants no longer take the same path through the reactor at different times. Instead, the substrate moves relative to the reactant sources. The reactants are no longer pulsed in the reactor. The reactants flow continuously or remain static because the substrate movement defines the reactant sequence. There are various versions of this alternative approach. The original idea of ALD with moving substrates between the various reactants was presented in a patent by Suntola and Antson in 1977 [9]. This scheme involved rotating the substrate between alternating reactant sources and vacuum pumping regions [9].

Variations on the original scheme of moving substrates with static or continuous reactants have developed in the last few years. This paper will review some of the main approaches that are based on this method. These designs can be divided in the general categories of: (1) gas source head with reactant slits [10, 11]; (2) gas bearings [12, 13]; (3) rotating sample cylinder [14]; and (4) moving through spatially separated reactants [15]. All of these methods have been used recently to deposit Al2O3 ALD films. These designs may be useful for continuous ALD roll-to-roll processing.
The implementation of ALD roll-to-roll processing is important for cost-effective ALD in many areas. One of the most important application areas is ALD coatings for gas diffusion barriers on polymer substrates [16]. These gas diffusion barriers on polymer are critical for flexible organic light emitting diode (OLED) displays and thin films solar devices. Recent results have shown that Al₂O₃ ALD coatings grown using TMA and H₂O form excellent gas diffusion barriers and yield effective WVTR values of ~5 x 10⁻⁵ g/m²/day at 38°C/85% relative humidity [16]. These WVTR values are upper limits to the true WVTR value because the glass lid controls gave the same WVTR values [16].

**DESIGN 1: GAS SOURCE HEAD WITH REACTANT SLITS**

Although the idea of performing ALD by moving substrates (or reactant sources) in space rather than alternating reactants in time is traceable to the patent by Suntola and Antson in 1977 [9], this idea did not reemerge until very recently. Levy and coworkers from Eastman Kodak demonstrated a working prototype of a gas source head with reactant slits [10]. This gas source head was able to oscillate back and forth on the substrate to perform ALD at atmospheric pressure. A schematic of their gas source head is shown in Figure 2. This apparatus was used to perform Al₂O₃ ALD and ZnO ALD. The Al₂O₃ ALD system displayed growth characteristics that were expected for this well-defined ALD process [17].

A subsequent report by Levy and coworkers called their moving gas source head design “spatial ALD” [11]. They also reported an improved system that incorporated “exhaust slots” in the gas source head. Using this design, they pointed out that high tolerance mechanical fixtures were needed to keep the substrate in close proximity to the coating head. As a design improvement, they allowed the substrate to approach the gas source coating head until the gas flow supported the substrate. The gas flow performed as a “gas bearing” in this adaption of the design. These subsequent design improvements also displayed the correct saturation behavior for Al₂O₃ ALD using TMA and H₂O as the reactants [11].

**DESIGN 2: GAS BEARINGS**

The use of a gas bearing to define the gap spacing between the gas source and the substrate has been further developed by Poodt and coworkers at TNO Science and Industry in The Netherlands [13]. In their implementation of the moving substrates (or reactant sources) in space, they employed a rotating substrate underneath their reactor head. The reactant sources were spatially separated on opposite sides of the reactor head. A sizeable exhaust zone surrounded each of the reactant sources. The gas bearings occupied most of the surface area of the reactor head. The gap between the gas bearing planes and the substrate was ~20 microns. In contrast, the reactant inlets had a gap distance of ~200 microns.

The gap between the gas source head and the substrate was reported to be 30 microns. The reactant slits were separated from each other by an N₂ inert gas isolation channel that prevented the mixing between the reactants. This inert gas is critical to prevent the reactants from mixing in the gas phase and depositing a film via chemical vapor deposition (CVD). The reactants and inert gas continuously flowed out of their slit sources during the ALD process. In the initial report of this design, there was no pumping in the gas source head. The reactants and inert gas exited the side of the gas source head and the ALD was performed at atmospheric pressure.

A schematic of the gas bearings and reactant and exhaust lines is shown in Figure 3. This schematic is not to scale. According to the descriptions in their paper [13], the gas bearings occupy much of the space of the reactor head. From the point of view of the rotating substrate, the gas bearing regions account for angular sections of ~120° on either side of the reactant sources. In addition, the gap spacings in Figure 3 are not to scale given the gap dimensions stated above. This rotating substrate design has been demonstrated using Al₂O₃ ALD. Linear growth of the Al₂O₃ ALD film thickness was observed with number of substrate rotations. The growth per cycle for Al₂O₃ ALD using TMA and H₂O was 0.12 nm as expected from previous studies.

![Figure 2: Gas source head with reactant slits.](image)

![Figure 3: Schematic of gas source head with gas bearings.](image)
Further developments employing gas bearings have been introduced by Kuznetsov and coworkers at Levitech in The Netherlands [12]. Their gas bearing design is intended to float wafers using gas bearings that are located on the top and the bottom of the wafer. With this “double” gas bearing design, the wafers do not have physical contact with any surface. The reactants are introduced on the top side of the wafer together with the N₂ gas for the gas bearing. Only a N₂ gas bearing is located on the bottom side of the wafer.

The Levitech design utilizes narrow channels for the reactants and N₂ gas [12]. There are no channels dedicated to exhaust gas or pumping. The reactants and N₂ gas flow across the wafer perpendicular to the substrate direction. This cross flow is then exhausted at the sides of the system. For Al₂O₃ ALD using TMA and H₂O, the ALD cycle is TMA, N₂, H₂O and N₂. The cell length required for this ALD cycle is 10-14 cm. They achieved the expected Al₂O₃ ALD growth rate of 0.12 nm per Al₂O₃ ALD cycle and reported a throughput higher than 2400 wafers per hour [12]. A modification of this design could be extended for continuous roll-to-roll processing.

DESIGN 3: ROTATING SAMPLE CYLINDER

There are also other alternative designs for performing ALD by moving substrates (or reactant sources) in space. The Beneq company in Finland has developed a reactor (Beneq TFS 200R) that can simulate the conditions for continuous ALD for roll-to-roll processing by placing a flexible substrate on a rotating cylinder [14]. The rotating cylinder is positioned in a reaction chamber and surrounded by regions that provide reactant, pumping and purging during rotation of the sample cylinder. A schematic of this design showing one ALD cycle per cylinder rotation is displayed in Figure 4.

This rotating sample cylinder design closely simulates roll-to-roll conditions and can be used to study ALD processes prior to roll-to-roll scale-up. The Beneq TFS 200R has a reported substrate speed of 300 m/min and deposition rates of up to 100 nm/min [14]. Most of the initial demonstration of this rotating sample cylinder design has been performed by Cameron and coworkers using Al₂O₃ ALD with TMA and H₂O as the reactants [18]. They have reported successful Al₂O₃ ALD processing and also observe some evidence for boundary layer effects that lead to additional Al₂O₃ growth at higher rotation velocities [18].

DESIGN 4: MOVING THROUGH SPATIALLY SEPARATED REACTANTS

Another different approach to performing ALD by moving substrates (or reactant sources) in space is based on moving the substrate through separate regions of precursor pressure and inert gas purging. This design is currently being pioneered by Lotus Applied Technology in Hillsboro, Oregon using TransFlex ALD™ [15]. A schematic illustrating this spatially separated reactants design is shown in Figure 5. This design is true roll-to-roll ALD processing with the polymer sheet traveling through precursor and N₂ purge gas regions on its way from the input roll to the take-up roll.

Using TransFlex ALD™, Lotus Applied Technology has reported web speeds of over 1 meter per second for the preparation of polymer films with high barrier properties [15]. Web speeds of over 10 meters per second have been reported for food packaging application. Both of these web speeds were obtained with a prototype 100 mm reactor. A benefit of the TransFlex ALD™ process is high precursor utilization. The ALD precursors do not share a common volume or pumping exhaust path. The precursors can be held in a static volume to improve reactant efficiency. The precursors can also be trapped or recycled to further improve reactant usage. Lotus Applied Technology has reported using TransFlex ALD™ for Al₂O₃ ALD and TiO₂ ALD processing [15].
MODEL EXPERIMENTS TO UNDERSTAND REACTOR PARAMETERS

Model experiments were performed to understand the dependence of roll-to-roll ALD on reactor parameters. A laboratory apparatus was constructed consisting of a fixed gas source coating head that sits above a substrate that is driven by a programmable stepper motor. The gas source coating head is composed of a series of rectangular channels that spatially separate the ALD reactions. This design is similar to the design reported by Levy and coworkers [11]. A cross-sectional schematic of the rectangular channels in the gas source head is shown in Figure 6.

Preliminary tests were conducted using He as a probe gas to demonstrate that operating conditions exist where the two reactant streams do not mix. Mixing of the reactants would yield Al₂O₃ CVD. The He probe gas was dosed into one of the reactant channels and the exhaust from the other reactant channel was monitored with a mass spectrometer to detect for He cross-diffusion. The detection of He was monitored versus TMA exhaust pumping and H₂O exhaust pumping with a fixed N₂ purge flow at various gap spacings. Results for a gap spacing of 100 microns are shown in Figure 7.

As the substrate moves under the gas source coating head, the channel sequence for each reactant is: precursor; exhaust; N₂ purge; and exhaust. The gas source head was built for 1.5 ALD cycles. Using Al₂O₃ ALD as a model system, the gas source head has the TMA reactant channel in the middle and the H₂O reactant channel on each side of the TMA reactant channel. This design allows for the deposition of two Al₂O₃ ALD cycles during one complete back-and-forth translation of the moving substrate.

A low conductance gap between the precursor and exhaust channels allows for nearly static reactant exposures and prevents intermixing of the reactants. A higher conductance gap was machined into the gas source head between the exhaust and purge channels to create a high flow entrainment region that further isolates the precursor channels. The spacing between the gas source head and substrate is fixed and can be controlled with micron precision. This apparatus can test how roll-to-roll ALD depends on the gap spacing, substrate speed, gas flow rates, and pressure difference between reactant and purge channels. An understanding of these process parameters is necessary for the successful implementation of continuous, large scale roll-to-roll ALD.

From the data in Figure 7, the optimum conditions were identified for no detectable He cross-diffusion. These conditions were then employed to deposit an Al₂O₃ ALD film on silicon wafers that were translated back and forth under the gas source head. These experiments revealed that maintaining a constant gap of 100 microns with sample translation is very difficult. The alignment of the plane of the translating silicon wafer and the bottom face of the gas source head needs to be extremely precise. Although the micrometers defined a constant gap of 100 microns in one position, very high tolerance is required to maintain this constant gap over translation distances of 4-5 cm.

The gas source head could deposit Al₂O₃ ALD films. However, the results were not easily reproducible. One of the best trials is shown in Figure 8. The Al₂O₃ ALD film thickness after 1000 cycles at 125°C was constant at ~880 Ångstroms across three large zones that were exposed to the gas source head. However, two regions between these three zones that corresponded to the location of the inlet to the pumping channel received less Al₂O₃ ALD coating. Attempts to fill these two regions by decreasing the pumping speed were not successful. Changing the pumping speed must have affected the other reaction parameters and possibly the gap spacing during translation.
Performing ALD during sample translation with a fixed gap has proven to be very difficult. The best machining tolerances may not be possible to maintain a fixed gap of 50-100 microns over translation distances of 4-5 cm. Gas bearing designs may be needed to obtain a gap spacing that adjusts for imperfections in alignment and deviations from planarity between the gas source head and the substrate.

CONCLUSIONS

A number of approaches are being developed towards the future goal of ALD for continuous roll-to-roll processing. This paper has reviewed a number of designs based on: a gas source head with reactant slits; gas bearings; a rotating sample cylinder; and moving through spatially separated reactants. All of these approaches have been demonstrated using Al₂O₃, ALD and other ALD systems. Many issues still need to be resolved before ALD for continuous roll-to-roll processing can become a reality. Progress over the last several years has been significant and additional development and understanding should lead to the commercialization of this important process.

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REFERENCES


