Spatial Atomic Layer Deposition: A Path to High-Quality Films on Continuous Substrates

David H. Levy, Roger S. Kerr, Shelby F. Nelson, Lee W. Tutt, and Mitchell Burberry

Eastman Kodak Company Rochester, NY 14650

Atomic Layer Deposition (ALD) is a film growth process proven for the fabrication of barrier layers, dielectric layers, and semiconductors. The technique produces high-density inorganic layers at reasonable process temperatures with excellent uniformity, thickness control, and conformality.

The basic ALD process involves exposing a substrate to a sequence of two or more reactive gases under the constraint that the substrate sees the reactive components one at a time. This approach allows each reactant to conformally saturate the substrate. In addition, the resulting film thickness can be well controlled because film growth occurs monolayer by monolayer.

Figure 1(a) shows a typical ALD process. In this process, the substrate is placed in a chamber and introducing and evacuating gases from the chamber varies the composition of the ALD gas. The sequence of gases seen by the substrate is shown in Figure 1(b). While this technique has been proven very effective at producing highquality films on discrete substrates, it is difficult to extend to large-area substrates due to the simultaneous requirement of a closed chamber and a rapidly varying reactant composition.



Figure 1: (a) A chamber ALD system, showing introduction of reactant gases (I) and (II) and exhaust; (b) A typical sequence of substrate gas exposures.

Figure 2(a) shows our alternative approach called spatial ALD (S-ALD). The S-ALD process employs the same set of reactive gases, although a coating head spatially locates these reactive gases. As a result, a substrate moving along these spatial regions sees the same sequence of reactive gases as in a typical chamber ALD process, but with the added benefit that gases flow at steady state.



Figure 2: (a) Schematic of the S-ALD coating head showing spatially located gas regions of inert and components (I) and (II) from Figure 1; (b) Gas exposure seen by a point Q as it moves along the coating head.

In our typical head designs, the separation between active channels (distance s in Figure 2(a)) is on the order of 5 mm. The critical requirement for this coating system is the ability to prevent mixing of gases I and II over this short distance as the substrate moves. In the spatial ALD technology, this is accomplished by the use of a slotted coating head as shown in Figure 3(a). The cross section in Figure 3(b) shows each source slot (upward solid arrows) surrounded by two exhaust slots (downward shaded arrows). With this approach, gas introduced from a particular source slot has the ability to be drawn away by an adjacent exhaust slot.



Figure 3: (a) S-ALD coating head showing gas source and exhaust slots; (b) Cross section view through the dotted plane showing gas entry into the coating region (upward solid arrows) and gas exhaust (downward shaded arrows).

While this basic approach can be successful, the main drawback is shown in Figure 4. When a substrate is maintained at a fixed distance mechanically from the substrate, the pressure field that drives gas introduced at a source slot to uniquely exit from the adjacent exhaust slots is very small, and thus gas will mix substantially.

The solution to this problem is to design the coating head to allow for very close approach of the substrate as shown in Figure 5. With this approach, the pressure gradients increase until that pressure is capable of supporting the substrate, at which point the substrate "floats" on the coating head. This provides relatively large pressure gradients that prevent gas from one channel from bypassing the adjacent exhaust slot and contaminating subsequent channels. This approach also has the side benefit of providing very small gas volumes in contact with the substrate, leading to effective scrubbing as the substrate moves.



Figure 4: Approximate gas flows in coating region with a large separation between the coating head and the substrate. The top feature shows approximate pressure variation along the coating head.



Figure 5: Approximate gas flows in coating region with a small separation between the coating head and the substrate. The pressure gradients between source and exhaust slots are increased.

Proper ALD growth is demonstrated by examining film thickness as a function of residence time (the time spent over each channel). Varying the substrate speed over the coating head varies residence time in our system. When a surface is exposed to one of the reactants during an ALD cycle, initially the surface will react with that material to form a partial monolayer. As the exposure time is increased, eventually a full monolayer of that reactant (or product) will be present on the surface. At this point, increased exposure leads to no increased growth because the substrate is saturated. Thus, if the amount of growth per ALD cycle is measured as a function of residence time, initially there will be an increase in the growth per cycle, but that will saturate to a known value for long residence times. Using a common reactant system to grow Al₂O₃, trimethylaluminum and water, saturating growth was observed. Furthermore, growth saturated for that system at approximately 1.2 Å per ALD cycle, which is consistent with chamber ALD results.

The system has been used to grow a number of materials. Al_2O_3 films used as dielectrics show leakage currents less than 10^{-8} A/cm² for 500 Å thick films. Zinc oxide semiconductor films show mobility greater than 15 cm²/Vs. These materials in combination have yielded stable thin-film transistors.

In conclusion, we have demonstrated a system with the ability to perform ALD depositions in open air on substrates in a lab environment. The resulting films grow with an expected ALD behavior and yield useful dielectric and semiconductor properties. Extension of this technology to larger substrates and web is underway.