Low temperature and roll-to-roll spatial Atomic Layer Deposition for flexible electronics

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Low temperature and roll-to-roll spatial atomic layer deposition for flexible electronics

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Spatial atomic layer deposition can be used as a high-throughput manufacturing technique in functional thin film deposition for applications such as flexible electronics. This; however, requires low-temperature processing and handling of flexible substrates. The authors investigate the process conditions under which low-temperature spatial atomic layer deposition of alumina from trimethyl aluminum and water is possible. The water partial pressure is the critical parameter in this case. Finally, our approach to roll-to-roll spatial atomic layer deposition is discussed. © *2012 American Vacuum Society*. [DOI: 10.1116/1.3667113]

I. INTRODUCTION

A. Spatial ALD for flexible electronics

The unique characteristics of atomic layer deposition (ALD), like its high conformality, film quality and thickness control down to the Ångstrom level, has made ALD to a well established technique in the micro-electronics industry.[1] An emerging field of applications for ALD is flexible electronics, including flexible displays, flexible organic light-emitting diodes and flexible (organic) solar cells. Flexible electronics are slowly but surely evolving from lab-scale to industrial production. This opens up new possibilities for ALD as a production technique for functional layers such as transparent oxide (semi)conductors[2] (e.g., ZnO) and moisture barriers[3] (e.g., Al_2O_3).

Atomic layer deposition has; however, a significant drawback; the deposition rate of conventional, time-sequenced ALD is very low and upscaling to large substrate sizes is complex, making it a high cost of ownership technique. In order to achieve high throughput numbers and reduce costs, there have been important recent developments regarding Spatial ALD.[4] Whereas for conventional ALD the precursors are dosed one by one, separated in time and by a purge step, in spatial ALD, the precursors are dosed simultaneously and continuously, but at a different physical location. The main advantage of spatially separating the half-reactions is that the purge steps between the precursor dosages in conventional ALD become obsolete. As a consequence, the deposition rate achievable is no longer limited by the accumulated individual cycle step times, but by the time required to form a monolayer by the two half-reactions plus the time it takes to move between half-reaction zones. In spatial ALD, it is essential to ensure a good separation of the half-reaction zones to prevent cross reactions that would lead to CVD conditions.

Recently, we presented a spatial ALD concept based on the gas-bearing technology.[5] In this concept, illustrated schematically in Fig. 1, the reactor is divided in separate zones exposing the precursors one by one to a substrate that moves underneath the reactor. Between and around the reaction zones, shields of inert gas separate the precursor flows. When operated properly, these gas shields can act as gas bearings, facilitating virtually frictionless movement between reactor and substrate. Furthermore, the gas bearings act as excellent diffusion barriers between the reaction zones, preventing cross-reactions and parasitic deposition on the reactor walls. This allows for very high deposition rates, while maintaining the typical ALD assets like film quality and conformality. Deposition rates exceeding 1 nm/s for alumina from trimethyl aluminum (TMA) and water have been achieved.

The use of spatial ALD for applications in flexible electronics also imposes some other boundary conditions on the deposition technique. First, it requires low-temperature processing (e.g., deposition temperature $<120\,°C$), as many polymer-based substrates and active layers are temperature sensitive. Second, the technique has to be capable of handling and processing of flexible substrates, either sheet-to-sheet or roll-to-roll.

B. Low temperature ALD

Thermal ALD of alumina from TMA and water at deposition temperatures down to $33\,°C$ has been investigated for instance by Groner *et al.*[6] They observed that ALD at these low temperatures is possible, but the density, refractive index and growth-per-cycle (GPC) reduce with decreasing temperature. This might be an indication that the quality of the films deposited at very low temperatures is compromised. A further observation is that with decreasing deposition temperature, the purge step after the water half-reaction has to increase significantly to ensure sufficient removal of water from the reactor (up to 180 s compared to a 2 s water

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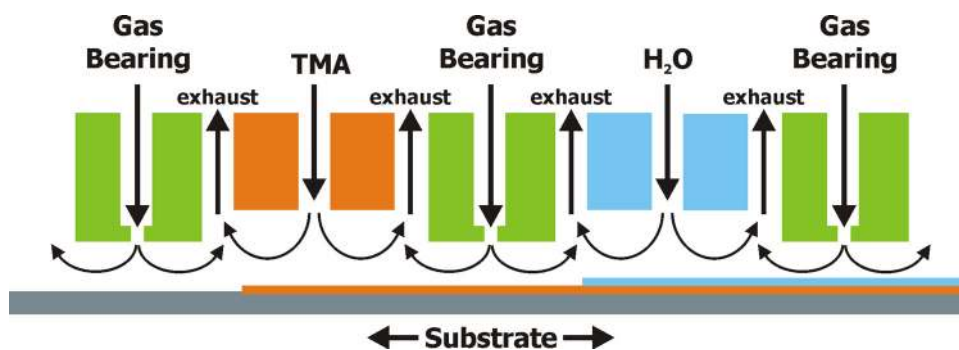
FIG. 1. (Color online) Schematic drawing of the spatial ALD reactor concept, where the TMA and water half-reaction zones are separated by gas bearings. By moving the substrate underneath the reactor, the two half-reactions will take place subsequently to form an Al_2O_3 monolayer.

exposure time at 33 °C). Water has a high sticking coefficient that can lead to multilayer adsorption of water on surfaces at low temperatures and sufficiently high partial pressures. All this excess water has to be removed before continuing the ALD cycle to avoid unwanted CVD reactions, requiring the reported long purge times. On the other hand, the water half-reaction was shown to be rate limiting in spatial ALD reactions, and quite a high water concentration as compared to TMA is required to obtain good depositions.[7] Thus, optimizing the water half-reaction process for low deposition temperatures is essential.

The relevant time scales in a spatial ALD reactor (i.e., the time available for the half-reactions and the time between the half-reactions) are fixed and determined by the dimensions of the injector as well as the relative movement speed between the substrate and the injector. So, it is not practical to individually change one of these timescales with respect to the others, for instance to mimic the prolonged purge times of Groner *et al.*[6] The alternative is to avoid multilayer water adsorption in the first place. To do this, accurate knowledge of the water adsorption behavior is required.

The adsorption isotherm of water on α-alumina at 296 K was determined by Al-Abadleh and Grassian.[8] It shows a complex behavior where three distinct regimes can be observed. Below 10% relative humidity (RH), the formation of a hydroxide monolayer on the alumina was observed. Between 10% RH and 70% RH, the formation of an ordered, icelike layer of water on top of the hydroxide layer was observed. Above 70% RH, water molecules adsorbed into disordered water layers. Therefore, it can be assumed that to avoid water multilayer adsorption, the water concentration should remain below 10% RH.

II. EXPERIMENT

The experiments were performed on a rotary spatial ALD reactor, described in detail in Ref. 5. Polished silicon wafers (15 cm diameter, 0.725 mm thickness) were used as substrates. Trimethylaluminum, TMA (electronic grade, AKZO HPMO) and water were used as precursors and were evaporated using bubblers. A total of 1000 ALD cycles was applied at a substrate rotation frequency of 120 rpm. The thickness and refractive index were determined with spectroscopic ellipsometry. All the relevant deposition parameters are listed in Table I.

III. RESULTS AND DISCUSSION

A. Low-temperature spatial ALD of alumina from TMA and water

The relative humidity is defined as the ratio between the water partial pressure and the water saturated vapor pressure, where the latter depends on temperature for which tabulated values are widely available. The water partial pressure, or water concentration, in the injector can be set by the water evaporator. A previously optimized water partial pressure for a deposition temperature of 200 °C was 123 mbar, which corresponds to a RH of ∼1%, well below 10% RH.[7] However, using these same settings at a deposition temperature of 75 °C, leads to a RH of 32%, which is much too high and leading to a deposition result as shown in Fig. 2. The film is much thicker than expected for ALD and extremely inhomogeneous (as indicated by the colors). Also some powder formation was observed.

Figure 3(a) shows a plot of the water partial pressure in the reactor versus reactor temperature (see Table I for the experimental settings). The solid line corresponds to 10% RH. Left of this line, RH >10% and right of this line RH <10%. For reference, the dashed line denotes the 1% RH line, the value corresponding to the optimized water partial pressure at a deposition temperature of 200 °C. The black data points (■) correspond to water partial pressures for which visually homogeneous depositions were obtained over the entire deposition area at deposition temperatures of 200, 150, 100 and 75 °C. Figure 3(b) shows the corresponding growth per cycle and refractive index, as determined by spectroscopic ellipsometry.

For temperatures down to 100 °C the optimized water partial pressures are below 10% RH and homogeneous depositions were obtained. Both the refractive index and GPC

TABLE I. TMA and water partial pressures and the corresponding relative humidity.

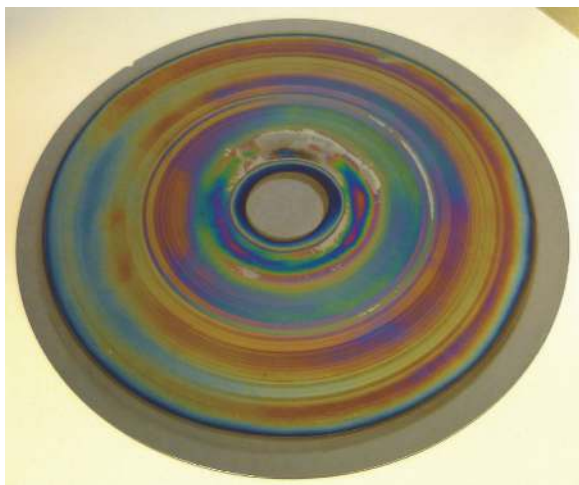| Deposition temperature (°C)	TMA partial pressure (mbar)	Water partial pressure (mbar)	Relative humidity (%)
200	3	155	1
150	3	100	2
100	3	61.5	6
75	3	61.5	16

FIG. 2. (Color online) 15 cm diameter silicon wafer after Al_2O_3 deposition with 1000 cycles of TMA and water in the rotary spatial ALD reactor at a deposition temperature of 75 °C, using a water partial pressure as optimized for a deposition temperature of 200 °C. The colors are indicative of thick and very inhomogeneous growth, with some powder visible near the center. This is indicative of a CVD effect caused by excess adsorbed water.

decrease slightly, which is in accordance with earlier reported results.[6] At 75 °C, a more or less homogeneous deposition could be achieved at a RH above 10%, but with these settings the GPC is very high and the refractive index quite low. Furthermore, this film appeared to have some porosity, which could be caused by powder formation during deposition.

With our spatial ALD reactor we were able to make good alumina films from TMA and water at deposition temperatures down to 100 °C, which is sufficiently low for most applications. At such low deposition temperatures it is required to decrease the water partial pressure with decreasing deposition temperature to avoid excess water adsorption, which would lead to CVDlike deposition conditions. However, as the rates of the half-reactions also decrease with decreasing deposition temperatures, the water partial pressure should not be too low or else incomplete half-reactions will occur, leading to undersaturated ALD and inhomogeneous depositions. Thus, low-temperature deposition is possible, but this calls for a careful balancing of the water partial pressure with deposition temperature. For many applications it is important to get this right to avoid for instance powder formation during deposition, as powder can have detrimental effects on layer quality.

B. Alternatives for water

There are alternatives for the TMA – water process, where the problem with the high water sticking coefficient can be avoided. For instance, ozone (O_3) can be used as an oxidant.[9] However, this is slightly more complex as it requires an ozone generator with a sufficiently high O_3 production rate. Particularly when going to high throughput applications where large amounts of ozone are required, this might become too costly. Furthermore, there is the risk that ozone is not compatible with organic materials.

Plasma enhanced ALD can also be used for deposition at reduced temperature.[10] Our reactor is operated at atmos-
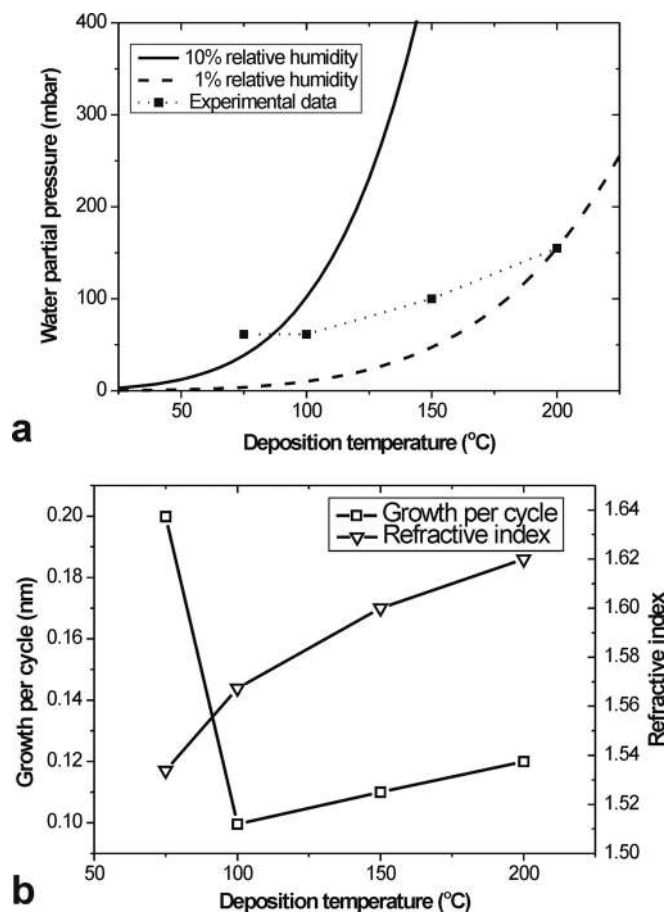

FIG. 3. (a) Optimized water partial pressures as a function of deposition temperature (■). The 10%RH and 1%RH lines are given as full and dashed lines, respectively. (b) The growth per cycle and refractive index as a function of deposition temperature corresponding to the partial pressures of Fig. 3(a).

pheric pressure, and the low-pressure plasmas typically used in PE-ALD cannot be used in our setup. However, it is possible to integrate an atmospheric pressure plasma source, using a dielectric barrier discharge to generate a plasma from helium. When a small amount of oxygen is introduced into the plasma, this can act as an oxidizing source instead of the water half-reaction at temperatures below 100 °C. We have used this for instance to create patterned depositions.[11] However, the chemistry of an atmospheric plasma is quite different from a conventional low-pressure plasma and its reactivity is too low to act as a full scale oxidation source. Alternatively, a He plasma can be used in a "plasma intermediated ALD" mode, as depicted in Fig. 4. In this manner, after each TMA-water cycle, the newly formed alumina interface is treated with a He plasma. The effects of such a treatment on the GPC and refractive index are shown in Fig. 5, where thermal spatial ALD is compared with plasma intermediated spatial ALD for temperatures of 100 °C and 75 °C. At 100 °C, the effect of the plasma treatment on the GPC and refractive index is marginal, as thermal ALD already gives good results, but at 75 °C, the GPC and refractive index return to expected values, resulting in a good quality and homogeneous film. Even at 50 °C there is a significant improvement, but still powder formation is present.
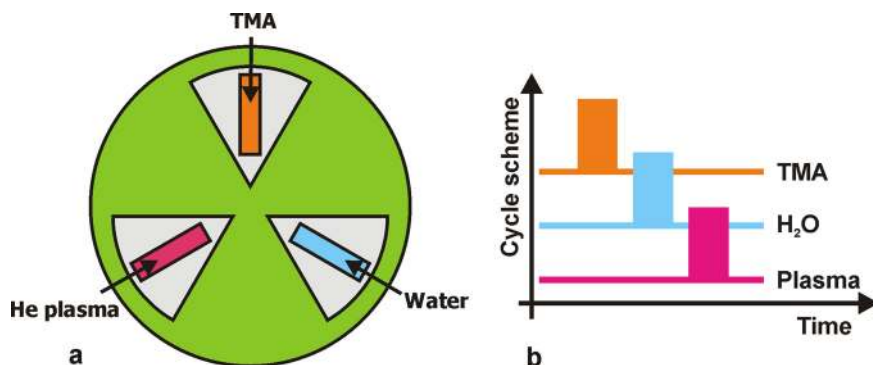
FIG. 4. (Color online) (a) Modified spatial ALD injector (bottom view) containing an atmospheric pressure plasma zone. If a substrate is rotated underneath in a clock-wise direction, each individual TMA—water cycle is followed by a plasma treatment, as shown in Fig. 4(b).

This approach looks promising when very low deposition temperatures are required, but still needs further refinement.

IV. CONCLUSIONS AND OUTLOOOK: ROLL-TO-ROLL SPATIAL ALD

Low-temperature deposition of alumina is possible with spatial ALD, which makes if feasible for using it for high throughput applications. The concept of spatial ALD is a flexible one, where various embodiments for specific applications can be designed, for small to large and for rigid and flexible substrates, including roll-to-roll. If ALD could be integrated in roll-to-roll processing, an obvious application would be the encapsulation of devices, creating a diffusion barrier against moisture and oxygen to protect the sensitive parts of these devices. It has been reported several times that with ALD of alumina, excellent moisture barriers can be made, with water vapor transfer rates (WVTR) down to 10^{-6} g/m^2/day.[3] We have tested the barrier properties of our low- temperature alumina using standardized calcium tests. Glass plates with metallic Ca was covered with 50 nm alumina films deposited at 100 °C were exposed to damp heat tests (50 °C, 85% RH) for several weeks. WVTR values comparable to literature values ($<10^{-5}$ g/m^2/day) were obtained in these tests.

We are currently developing a roll-to-roll spatial ALD reactor, consisting of a central drum that contains one or more combinations of TMA and water half-reaction zones,[12] as illustrated in Fig. 6. These zones are separated and surrounded by nitrogen gas bearings. The foil to be coated is
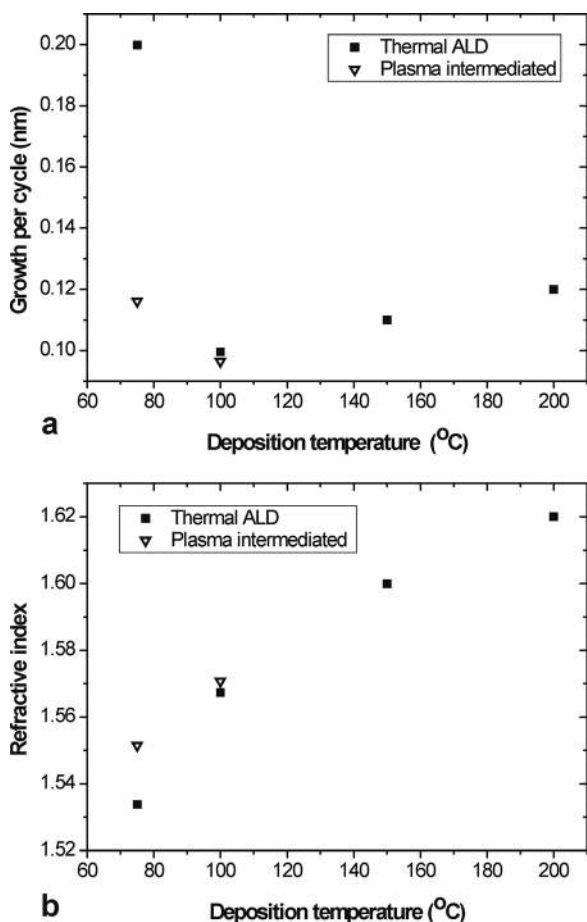

FIG. 5. Growth per cycle (a) and (b) refractive index as a function of deposition temperature for thermal spatial ALD (■) and plasma intermediated thermal spatial ALD (▽).
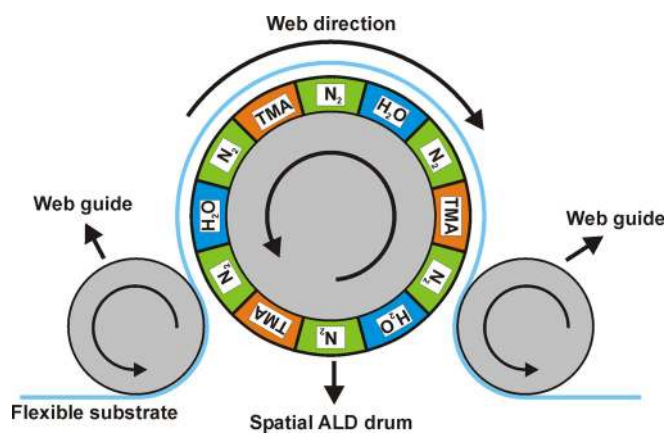

FIG. 6. (Color online) Schematic of the roll-to-roll concept currently under development at TNO, consisting of a central rotating drum that contains one or more combinations of TMA and water half-reaction zones. These zones are separated and surrounded by nitrogen gas bearings. The foil to be coated is pulled over this drum, where the gas bearing ensures that the foil is kept at a fixed distance from the surface of the drum. If the foil is then moved over the drum, ALD deposition will take place, where the total thickness is determined by the rotation frequency of the drum in combination with the movement speed of the foil.

pulled over this drum, where the gas bearing ensures that the foil is kept at a fixed distance from the surface of the drum (typically tens to hundreds of micrometers). If the foil is then moved over the drum, ALD deposition will take place, where the total thickness is determined by the number of half-reaction zone pairs that the foil passes. However, higher deposition rates can be achieved if the drum is rotated in the opposite direction of the movement direction of the foil. In this manner, the total thickness is determined by the rotation frequency of the drum in combination with the movement speed of the foil. The main benefit of this roll-to-roll concept is that there is no mechanical contact between the deposition side of the foil and the reactor and that there is a minimum of moving parts. This minimizes contamination of the foil with particles that would lead to pinholes in the deposited films and; consequently, deteriorates the barrier function. Furthermore, there is flexibility in the choice of substrate thickness and material as well as the total thickness of the deposited films. The latter can be tuned by varying the central drum rotation frequency.

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