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Facile Encapsulation of Oxide based Thin Film Transistors by Atomic Layer Deposition based on Ozone

*Morteza Fakhri, Nikolai Babin, Andreas Behrendt, Timo Jakob, Patrick Görrn, and Thomas Riedl**

Thin film transistors (TFT) based on transparent amorphous oxide semiconductors (TAOS) have been the object of tremendous interest during the past few years.[1–3] TFTs based on TAOS channel semiconductors have been evidenced to show a high carrier mobility even in the amorphous phase.[4,5] Therefore, applications like high performance pixel driver electronics for high resolution displays and large-area flexible electronic systems are envisaged.[6,7] Commonly, metal-oxide based TFTs are sensitive towards ambient gases like oxygen and water.[8,9] The adsorption of oxygen at the channel surface crucially affects the TFT characteristics.[10–12] Similarly, the transfer characteristics as well as the hysteresis of TFTs are influenced by adsorbed water.[13,14] At the same time, the degradation of device parameters under illumination and bias stress is accelerated in the presence of ambient gases.[15] Therefore, a proper encapsulation of the metal-oxide based TFT is mandatory in order to reduce the influence of ambient gases and to achieve stable devices. Common techniques for the preparation of gas diffusion barrier layers are chemical vapor deposition (CVD), sputtering and atomic layer deposition (ALD).[16–19] Among them, ALD has been shown to yield barrier layers with outstandingly low permeation rates for water and oxygen.[20,21] However, encapsulation of metal-oxide TFTs with conventional ALD using water as oxygen source is found to substantially alter device characteristics, most prominently the threshold voltage.[19] Post-annealing of the devices in oxidizing atmosphere is often necessary to recover the original transistor properties. This requirement for post processing is time and energy consuming and adds substantially to production complexity and cost.

In this report, we demonstrate a facile encapsulation approach for metal-oxide based TFTs using ozone as the oxidizing agent in an ALD process. In stark contrast to the established water-based ALD processes, ozone as in-situ source for oxygen prevents the shift of threshold voltage during the deposition of the encapsulation layer. Thus, no post-deposition annealing of the encapsulated TFT in oxygen atmosphere is required to restore its characteristics before encapsulation. Moreover, the hysteresis present in un-encapsulated transistors can be permanently suppressed by the ALD encapsulation. It is especially important to stress, that we are able to show that this approach is of general validity for various ALD encapsulation materials (e.g. Al_2O_3, TiO_x, ZrO_2) and applies to several important metal oxide channel semiconductors, like zinc-tin-oxide (ZTO) and indium-gallium-zinc-oxide (IGZO).

A typical transfer characteristic of a ZTO transistor (channel thickness: 50 nm) before (square symbols) and after (circle symbols) ALD encapsulation using a conventional TMA and water process is illustrated in **Figure 1**. The threshold voltage (V_{th}) of the device is severely reduced upon encapsulation by more than 25 V from 3.1 V down to -23 V. Opposed to that, the saturation mobility $\mu_{sat} \approx 7$ cm^2(Vs)$^{-1}$ remains unaffected. In previous reports, the reduction of V_{th} in a similar ALD process has been related to the removal of oxygen during the process.[22] TMA and other metal-organic ALD precursors are known to be strong Lewis acids. The oxygen molecule itself is also a Lewis acid, and it is well known that TMA does not chemically react with neutral O_2.[23] On the other hand, negatively charged oxygen at the surface of a metal oxide is substantially less Lewis acidic and has even been classified as Lewis base.[24,25] As a result, a chemical reaction of the Lewis acid TMA with the negatively charged oxygen becomes possible. A detailed discussion of the interaction of a Lewis acid-base pair on oxide surfaces has been reported elsewhere.[24,25]

With regard to the TFT, adsorbed oxygen at the surface of a metal oxide channel leads to a negative surface charge and a depletion layer due to trapping of electrons from the semiconductor channel.[11] Detrapping of electrons after removal of these oxygen related states leads to an increase of free charge carrier density in the TFT channel and consequently to a lowered threshold voltage.[18,22] This effect has been generally observed for other transistors with a TAOS channel, like those based on IGZO.[19] Commonly, a post-treatment step like annealing of the encapsulated TFT in oxidizing atmosphere is, therefore, necessary in order to re-establish the adsorbed oxygen at the TFT channel and thereby to reduce the free charge carrier density and recover the original device characteristics. As an example, Figure 1 (triangular symbols) includes the transfer characteristics of the encapsulated TFT after annealing at 200 °C for 10 min in air. The original value of the threshold voltage (V_{th} = 3.1 V) before encapsulation is almost fully recovered by this annealing step. Obviously, annealing in air leads to re-adsorption of oxygen, as a result of the thermally activated increase of gas permeability of the Al_2O_3 barrier at elevated temperatures.[20] Interestingly, the hysteresis is significantly reduced due to the encapsulation compared to the initial value. This effect can be accounted to the desorption of water during the encapsulation process in vacuum. Recent studies

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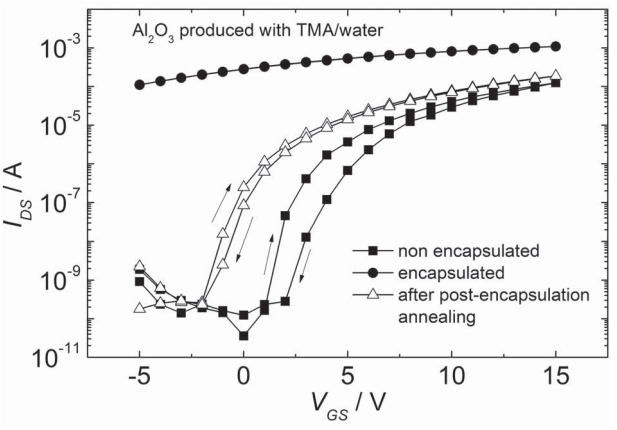

Figure 1. Transfer characteristics of encapsulated TFTs using ALD with water as oxidizing agent: device characteristics before encapsulation (squares), after encapsulation (circles), after post-encapsulation annealing at 200 °C for 10 min in air (triangles).

have already demonstrated the impact of water on the hysteresis of ZTO TFTs.[14,26]

From an application point of view, it would be extremely desirable to avoid the requirement for any costly energy- and time-consuming post-treatment process. We therefore demonstrate the encapsulation of metal-oxide based TFTs using ALD barriers prepared with ozone instead of water as oxidizing agent. We will show that, thereby, we can overcome the requirement for any post-encapsulation treatment. In general, ALD processes based on ozone are well established and the ALD reaction scheme of the TMA and O_3 process has been clarified before, e.g. ref.[27]. However, as of yet, ALD barrier layers based on ozone have not yet been used for the encapsulation of metal-oxide TFTs. **Figure 2** illustrates the transfer characteristics of a TFT before (square symbols) and after (circle symbols) the encapsulation with a TMA/O_3 process. In contrast to the device that is encapsulated using water, the threshold voltage is only negligibly shifted from 2.7 V to 1.3 V upon encapsulation. As opposed to the TMA/H_2O process the in-situ supply of oxygen in the TMA/O_3 process allows for re-adsorption of oxygen at the TFT channel surface and thereby a threshold voltage similar to that of the TFT before encapsulation is preserved. It is worth to note, that the mobility, μ_{sat} = 8 $cm^2(Vs)^{-1}$, is almost unaffected while the hysteresis of the encapsulated TFT is almost entirely eliminated. A detailed summary of the TFT properties before and after encapsulation using TMA/O_3 is given in the supporting information (Table S1).

To study the effect of ozone in this process, the TFT has been in-situ characterized during the first cycles of the ALD encapsulation process. It is essential to note beforehand, that the ozone treatment of TFTs without encapsulation leaves their device characteristics unchanged.

Figure 3(a) illustrates the threshold voltage V_{th} of the TFT upon TMA (t_{pulse} = 200 ms) and ozone exposure. As expected, V_{th} is strongly reduced upon exposure to a single TMA pulse. However, the threshold voltage fully recovers after introducing ozone into the reactor. Notably, the time constant of this process (τ) is smaller than the time resolution (Δt) of the experiment ($\tau << \Delta t$ = 1 min). Obviously, ozone leads to a fast adsorption of oxygen at the semiconductor surface, which consequently increases V_{th} towards the original value. Strikingly, a similarly fast re-adsorption of oxygen cannot be achieved if the device is exposed to O_2 instead of ozone. Figure 3(b) depicts V_{th} as a

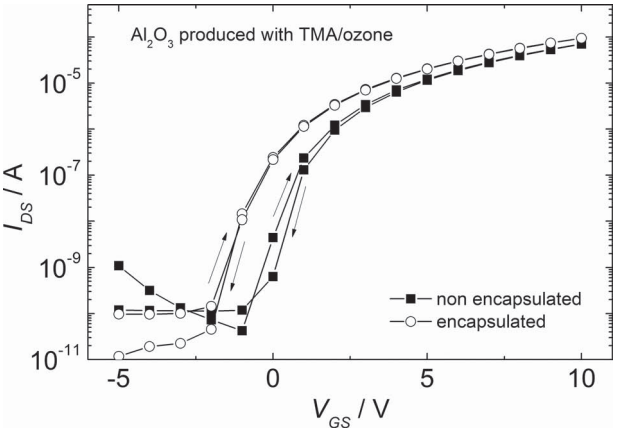

Figure 2. Transfer characteristics of encapsulated TFTs using ALD with ozone as oxidizing agent: characteristics before encapsulation (squares) and after encapsulation (circles).

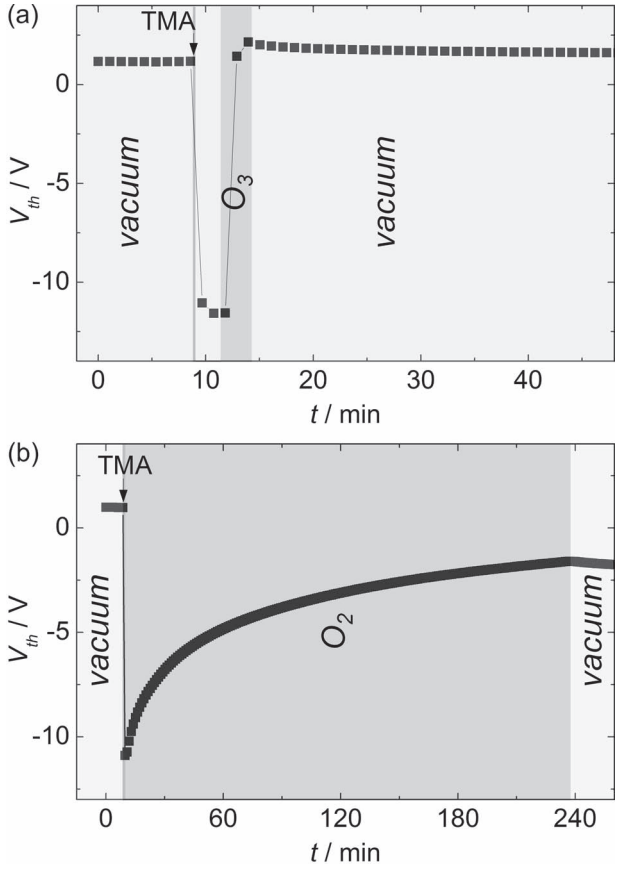

Figure 3. Time dependence of V_{th} upon TMA exposure (t_{pulse} = 200 ms) and subsequent O_3 exposure (t_{O3} = 2 min) (a), or subsequent O_2 exposure (b), respectively.

function of time upon O_2 exposure. The adsorption of oxygen due to O_2 exposure (p_{O2} = 2 mbar) reveals a time constant (τ = 1.7 h) several orders of magnitude larger than that seen upon O_3 exposure (τ << 1 min). This difference in adsorption time constant can be explained by the higher electron affinity of ozone compared to that of O_2[28] which is expected to lead to a more efficient capture of an electron from the semiconductor channel.

In the following we have studied the in-situ diffusion processes during an encapsulation process based on both water and ozone. We first designed an experiment to obtain an estimate for a barrier thickness of Al_2O_3 that is sufficient to hinder TMA diffusion to the TFT channel surface. To this end, we study a bi-layered barrier as shown in the inset of **Figure 4**(a). Specifically, the overall Al_2O_3 encapsulation layer has a thickness of d = 50 nm and is composed of an Al_2O_3 layer prepared from TMA/ozone (thickness d_{O3}) and a subsequently deposited Al_2O_3 layer prepared from TMA/water (thickness d_{H2O}). Figure 4(a) depicts the change of the threshold voltage ΔV_{th} upon encapsulation in dependence on the film thickness d_{O3}. As discussed, a barrier layer prepared only from TMA/water (d_{O3} = 0 nm) leads to a strong negative shift of the threshold voltage by about 20 V. On the contrary, using only a 1 nm thick Al_2O_3 interlayer produced with TMA/ozone already substantially reduces the threshold voltage shift to only ΔV_{th} = –2.5 V. An increase of the interlayer thickness (d_{O3}) shows no substantial further effect. These results tell us, that already a 1 nm thin Al_2O_3 barrier prepared by TMA/ozone is able to protect the TFT channel against precursors used in a subsequent ALD process. This would be relevant for a subsequent ALD process in which ozone does not work as oxidizing agent. Our results of this experiment also show that the severe shift of the threshold voltage as seen in a TMA/water ALD process already happens within the first nanometer of deposition. Importantly, the data presented in Figure 4 (a) also tells us, that potentially trapped charges in the deeper volume of the encapsulation layer prepared from TMA/water do not significantly affect V_{th}, as in the presence of the 1 nm thin Al_2O_3 barrier (TMA/ozone) ΔV_{th} is independent of the thickness d_{H2O}. In a similar sense, as ΔV_{th} is independent of the distance ($d_{O3} \geq 1$ nm) of the extra interface within the bi-layer from the TFT channel, we can rule out a significant contribution of trapped charges at this interface.

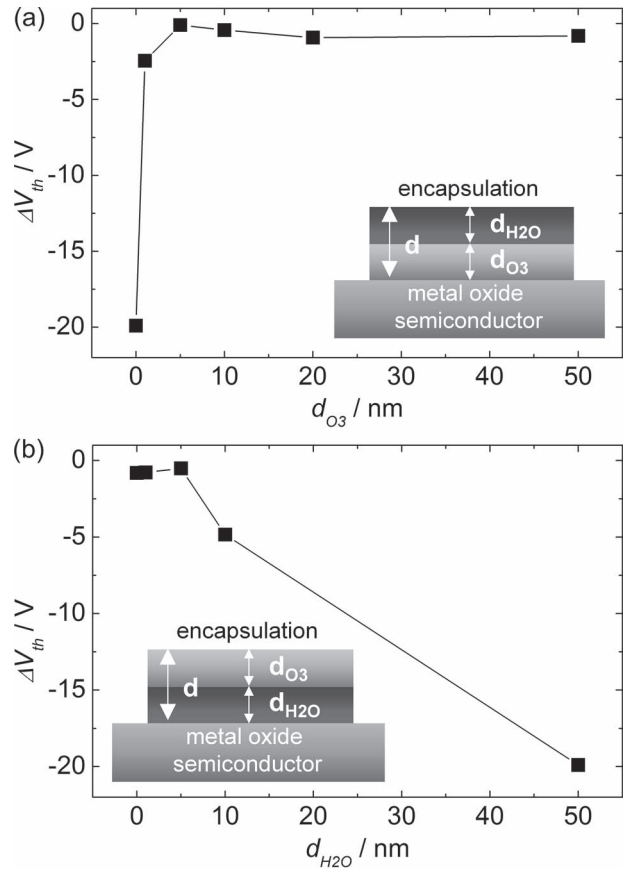

Figure 4. Change of the threshold voltage ΔV_{th} upon encapsulation with a bi-layered barrier. d_{O3}, d_{H2O} represent the thickness of the Al_2O_3 layer produced with ozone and water as oxidant agent, respectively. The overall Al_2O_3 layer thickness is kept at $d = d_{O3} + d_{H2O}$ = 50 nm. (a) Barrier layer using first ozone and then water as oxidizing agents. (b) Encapsulation by flipping the layer sequence and using first water and then ozone as oxidizing agent.

In an analogy to the experiment above, the sequence of the TMA/water and TMA/ozone layers is now flipped. From this set of samples, we intend to learn if the ozone used in the TMA/ozone process can diffuse through the already existing Al_2O_3 layer. As above, the TFT is encapsulated by a bi-layer, this time starting with TMA/water (thickness d_{H2O}) and a subsequent Al_2O_3 layer made with TMA/ozone (thickness d_{O3}) (see inset of Figure 4 (b)). Again, the overall barrier thickness is kept constant ($d = d_{O3} + d_{H2O}$ = 50 nm). Figure 4 (b) illustrates the change of the threshold voltage ΔV_{th} upon variation of d_{H2O}. While ΔV_{th} is almost zero for $d_{H2O} < 5$ nm, a steady decrease of ΔV_{th} can be observed for $d_{H2O} > 5$ nm. In case of a barrier layer produced with TMA/water only (this means d_{H2O} = 50 nm), the threshold voltage is strongly shifted to -20 V, as discussed before. These results demonstrate that ozone can diffuse through an already existing (thin) Al_2O_3 layer. It can supply oxygen to the TFT surface and consequently recover the threshold voltage of the TFT before encapsulation. The possibility to recover the threshold is more and more limited with increasing thickness d_{H2O} of the already existing Al_2O_3 layer due to hampered diffusion of ozone to the TFT channel surface. This experiment clearly supports our above conclusion, that ozone really is responsible for the recovery of the initial TFT characteristics by the re-establishment of negatively charged oxygen at the TFT channel surface. Obviously, a similar mechanism is not possible for H_2O.

It is important to note, that our finding has a general character and applies for encapsulation layers other than Al_2O_3 and other metal-oxide channel semiconductors. **Table 1** summarizes the shift of the threshold voltage ΔV_{th} and the reduction of the hysteresis V_h upon encapsulation with Al_2O_3, TiO_2 and ZrO_2. If IGZO is used as channel material instead of ZTO, a shift of threshold voltage is also found upon encapsulation using an ALD process based on water. We want to note that the shift of V_{th} upon encapsulation is smaller than found for the ZTO devices. This may be attributed to different preparation conditions of the ZTO and IGZO channel semiconductor. The MF sputter deposition used for IGZO may lead to a substantially reduced density of negatively charged chemisorbed oxygen

Table 1. Shift of threshold voltage ΔV_{th} and reduction of hysteresis ΔV_h (with reference to the initial hysteresis voltage before encapsulation $V_{h,0}$) upon encapsulation with various dielectrics using water or ozone as oxidizing agent. Note, that V_h can only be determined for devices encapsulated using ozone, where a reasonable transfer characteristic is detected.

Encapsulation material	Channel material	ΔV_{th} [V]		$\Delta V_h/V_{h,0}$
		water	ozone	ozone
Al_2O_3	–	–20	–1.4	–70%
TiO_2	ZTO	–29.5	–1.8	–40%
ZrO_2	ZTO	–9	–1.4	–100%
Al_2O_3	IGZO	–1.1	0.1	–50%

than in the case of the RF sputtered ZTO channels. Nevertheless, as reported for ZTO, the shift of V_{th} in the IGZO TFTs can be entirely avoided when they are encapsulated using TMA and ozone instead of TMA and water.

Finally, we have investigated the long-term behavior of our ALD encapsulated devices based on ozone. For this purpose, we have measured the transistors over a time period of about 40 days. **Figure 5** shows the threshold voltage V_{th} and the hysteresis V_h vs. time. The first data point denotes the TFT characteristics before encapsulation, while the further data points are measured after encapsulation and storage in a dark air ambient at room temperature. The outstanding stability of V_{th} and the small residual hysteresis of only 80 mV, reflects the excellent barrier characteristics of the Al_2O_3 encapsulation layer prepared with TMA and ozone against the penetration of oxygen and moisture. This finding is of particular importance for a stable operation of metal oxide based TFTs unaffected by ambient gases.

In conclusion, we have shown that the encapsulation of TFTs based on a metal-oxide semiconductor with a metal-oxide gas diffusion barrier using conventional atomic layer deposition (ALD) with water as oxygen source is found to substantially alter device characteristics. Specifically, a strong reduction of the threshold voltage is encountered, as a result of the reaction

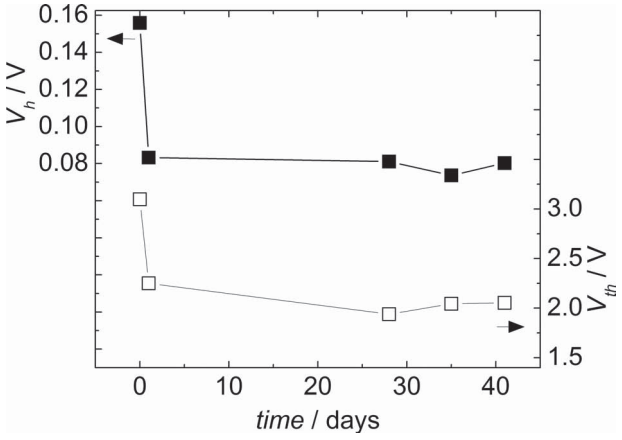

Figure 5. Long-term behavior of the threshold voltage V_{th} and hysteresis V_h of devices encapsulated with 50 nm of Al_2O_3 (prepared with TMA/ozone) vs. time. First data point indicates device characteristics before encapsulation.

of the Lewis-acidic metal-organic precursors with negatively charged chemisorbed oxygen. Therefore, post-annealing in oxidizing atmosphere is typically required to partly recover the original TFT characteristics. To overcome this issue, we have demonstrated a simplified encapsulation, using ozone instead of water as an oxygen source in a low-temperature ALD process, which leaves the threshold voltage unaltered and the hysteresis permanently reduced. Thereby, any costly energy- and time-consuming post-treatment processes can be avoided. Remarkably, this concept is widely applicable to various encapsulation materials (e.g. Al_2O_3, TiO_2, ZrO_2) and metal-oxide channel semiconductors (e.g. zinc-tin-oxide (ZTO), indium-gallium-zinc-oxide (IGZO)).

Experimental Section

The staggered bottom gate TFTs in this study are fabricated on glass substrates coated with a 200 nm indium tin oxide (ITO) gate electrode and a 220 nm thick dielectric composed of Al_2O_3 and TiO_2 multilayers, prepared by atomic layer deposition. The ZTO channel layer has been deposited by RF-magnetron sputtering at room temperature. A detailed preparation procedure is given in ref. [29]. The IGZO TFTs were fabricated by depositing the channel layer with MF-magnetron sputtering at room temperature in a mixed sputtering atmosphere of argon and oxygen (p_{O2} = 3%). All devices were post-annealed at 400 °C. Finally, the TFTs are encapsulated with a 50 nm thick Al_2O_3 layer, produced by ALD with water or ozone as oxidizing agent at 80 °C (in a Beneq TFS 200 ALD system). As metal-organic precursors we used trimethylaluminum (TMA) for Al_2O_3, titaniumisopropoxid for TiO_2, and tetrakis(dimethylamido)zirconium(IV) for ZrO_2. All experiments have been done in darkness, to avoid effects of illumination on the device characteristics [30].

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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