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Citation for published version (APA):

Jinesh, K. B., Lamy, Y., Wolters, R. A. M., Klootwijk, J. H., Tois, E., Roozeboom, F., & Besling, W. F. A. (2008). Silicon out-diffusion and aluminum in-diffusion in devices with atomic-layer deposited La₂O₃ thin films. *Applied Physics Letters*, 93(19), 192912-1/3. [192912]. <https://doi.org/10.1063/1.3025850>

DOI:

[10.1063/1.3025850](https://doi.org/10.1063/1.3025850)

Document status and date:

Published: 01/01/2008

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Silicon out-diffusion and aluminum in-diffusion in devices with atomic-layer deposited La_2O_3 thin films

K. B. Jinesh,^{1,a)} Y. Lamy,¹ R. A. M. Wolters,¹ J. H. Klootwijk,² E. Tois,³ F. Roozeboom,¹ and W. F. A. Besling¹

¹NXP Semiconductor Research, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands

²Philips Research, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands

³ASM Microchemistry Ltd., Vin Auerin Katu 12 A, FIN-00560 Helsinki, Finland

(Received 16 July 2008; accepted 23 October 2008; published online 12 November 2008)

The use of aluminum as an electrode in metal-insulator-semiconductor devices containing lanthanum oxide is impaired by unacceptable leakage current levels. Time of flight secondary ion mass spectroscopy depth profiling shows a significant amount of silicon out-diffusion from the substrate and aluminum in-diffusion towards the oxide. By using titanium nitride as the electrode, the silicon out-diffusion is suppressed, which improves the device performance. This indicates that, despite the larger coordination number of the lanthanum ions in the oxide, aluminum acts as a sink for silicon, thus driving the out-diffusion of silicon. © 2008 American Institute of Physics.

[DOI: [10.1063/1.3025850](https://doi.org/10.1063/1.3025850)]

The International Technology Roadmap for Semiconductors proposes La-based oxides as promising next generation dielectrics due to their relatively high permittivity (20–27), good electrical characteristics and potential for equivalent oxide thicknesses ≤ 1 nm, larger band gap (5.8–6.5 eV) compared to thermal silicon oxide, and even better thermodynamic stability than aluminum oxide.^{1–4} From a processing perspective as well, La_2O_3 is complementary metal-oxide-semiconductor compatible that can be deposited with various techniques such as atomic layer deposition,⁵ which gives excellent step coverage and deposition control on various topologies.

For the electrical characterization of lanthanum oxide (La_2O_3), usually metal-insulator-silicon (MIS) devices are fabricated on silicon substrates with aluminum as the top electrode. Recent studies suggest that silicon atoms diffuse outwards from the substrate through La_2O_3 towards the high- k electrode interface.⁶ In this letter, we report on the extent of silicon out-diffusion and aluminum in-diffusion in MIS devices with La_2O_3 as an intermediate dielectric.

Thin La_2O_3 films were deposited on p -type (3–10 Ω cm) 150 mm Si (100) substrates at 300 °C in an ASM PULSAR® 2000 reactor using La(thd)₃ and ozone as precursors, as described before.⁷ The deposited film thickness was 14 nm, as determined from spectroscopic ellipsometry and transmission electron microscopy. For the electrical characterization of the devices, 500 nm of aluminum and 100 nm TiN were sputter deposited on the oxide layer, respectively, at temperatures around 100 °C to exclude the deposition process from triggering silicon out-diffusion. Al electrodes with different sputtering powers were also examined, with comparable results. The aluminum and TiN top electrodes were patterned using standard lithography and etching. Electrical measurements were done using an Agilent 4155C semiconductor parameter analyzer and an HP multi-frequency LCR meter.

Compositional depth profiles were acquired with time of flight secondary ion mass spectroscopy (TOFSIMS) with an ION-TOF-SIMS IV instrument using Cs^+ ions as sputtering ions in negative mode (detection of negatively charged secondary ions). TOFSIMS offers the major advantage of using parallel acquisition; therefore, the entire mass spectrum can be stored during each cycle of the depth profile. Depth profiles can be subsequently reconstructed from the raw data files which allow reconstruction of a three-dimensional (3D) stoichiometric map of the layers. This is ideal for detecting unknown contaminants at buried interfaces or for studying

FIG. 1. (Color online) TOFSIMS images of Al/ La_2O_3 /Si structures: (a) silicon ion signal on the top aluminum electrode; (b) 3D view of silicon diffusing through the oxide and aluminum layers; (c) Al– La_2O_3 interface after sputtering off Al; (d) 3D La-ion mapping of the La_2O_3 layer; (e) Al-ion mapping of electrode top surface; (f) 3D Al-ion mapping of the device. The surface scan area is $70 \times 70 \mu\text{m}^2$ and the depth covers the thickness of the electrode (500 nm Al or 100 nm TiN) and the oxide (14 nm). Note that the thickness is not in scale with the surface area.

^{a)}Author to whom correspondence should be addressed. Electronic mail: k.b.jinesh@nxp.com.

FIG. 2. (Color online) Typical profiles of Al, La, O, and Si TOFSIMS ion counts across Al/La₂O₃/Si structures.

many elements simultaneously. TOFSIMS depth profiling was performed

Figure 1 shows a 3D TOFSIMS stoichiometric mapping of the as-deposited device, as constructed by successive sputter removal of the layers. Figure 1(a) shows the scan of the top Al electrode, showing the location of the silicon precipitates that appear as bright yellow spots on the top surface. Figure 1(b) shows silicon spikes protruding from the substrate through the oxide layer and into the top of the aluminum electrode. Figure 1(c) shows a La scan of the Al–La₂O₃ interface after sputtering off the aluminum. The interface appears to be very nonuniform. The 3D map in Fig. 1(d) shows that the Si–La₂O₃ interface is even rougher. Figure 1(e) shows the scan of the top aluminum electrode surface constructed from the aluminum signal. The 3D mapping of the device, reconstructed by the Al ions as shown in Fig. 1(f), demonstrates a bright top surface and a bright Al–La₂O₃ interface. The enhanced brightness in both areas is indicative of the presence of aluminum in oxidic form (probably Al₂O₃).

Figure 2 shows the TOFSIMS ion count profiles of Al, La, O, and Si ions across the Al/La₂O₃/Si MIS structure along the silicon spikes appearing through the oxide (Fig. 1) as a function of sputter time. Strikingly, the aluminum and silicon signals extend beyond their interface with the La₂O₃ layer, which shows that aluminum diffuses into the La₂O₃ layer and silicon diffuses from the substrate through La₂O₃ towards the aluminum electrode. In contrast to the earlier observations by Pan *et al.*,⁶ the silicon atoms are not localized at the interface between Al and La₂O₃ but dissolve in aluminum and reach even the top electrode, forming Si precipitates on the electrode. In addition, the Al₂O₃⁺ signal has a longer but steeper tail extending beyond the Al–La₂O₃ interface, possibly indicating the formation of Al₂O₃ at the inter-

FIG. 3. (Color online) TOFSIMS Si-ion mapping images of TiN/La₂O₃/Si structures showing very uniform layers and less silicon out-diffusion: (a) no silicon signal detected on the TiN electrode; (b) cross-section showing Si atoms accumulating at the TiN/La₂O₃ interface; (c) no Si spikes visible from the substrate.

FIG. 4. (Color online) Depth profile showing less silicon out-diffusion in the TiN/La₂O₃/Si device.

face. In addition, it is very likely that the aluminum atoms diffused into the oxide have formed lanthanum aluminate.

The TOFSIMS experiments demonstrate clearly that silicon diffuses through the La₂O₃ layer and 500 nm thick aluminum electrode. The Si atoms form precipitates on the aluminum surface even at room temperature. Rare-earth metal oxides, especially lanthanum oxide, have relatively larger cationic radii and larger coordination numbers in the solid compared to other metal oxides. In other words, the film is less dense compared to, say, Al₂O₃. This allows silicon out-diffusion from the substrate, forming lanthanum silicate in the film.⁸ The silicon spikes are not visible in the samples with the TiN top electrode, as shown in Fig. 3. This indicates that silicon out-diffusion due to the higher coordination number of La₂O₃ is enhanced significantly by the presence of the Al electrode on top. In a direct Si–Al contact, up to 1 at. % of silicon can be dissolved by Si out-diffusion.⁹ The relative

FIG. 5. (Color online) (a) J - E characteristics of MIS capacitors with aluminum and TiN electrodes. Aluminum as the top electrode causes much higher leakage current. (b) Weibull distributions of the breakdown electric field of La₂O₃ measured for both electrodes.

Si-ion counts compared with the aluminum signal in Fig. 2 and the TiN signal in Fig. 4 show that silicon out-diffusion is significantly lower with TiN as the top electrode. Thus, the solid solubility of Si in Al acts as a sink for Si in this diffusion process, whereas this force driving the Si transport is absent for TiN. The appearance of the silicon spikes is rather surprising since the lanthanum oxide film is amorphous and therefore there should not be any preferential path for the silicon out-diffusion. As the diffusion of Si in Al will be faster along grain boundaries, it must be the grain boundaries in the aluminum electrodes that direct the silicon atoms to diffuse through specific locations.

The effects of these interdiffusions are reflected in the leakage current through the device as seen in the current density–electric field (J - E) plot shown in Fig. 5(a). Upon utilizing an aluminum electrode, the leakage current is orders of magnitude higher in comparison with the TiN electrode (at 4 MV/cm the leakage currents are 10^{-3} and 10^{-7} A/cm², respectively). Please note that the difference in leakage current is partially due to the higher work function difference between aluminum and TiN to lanthanum oxide. After a forming gas anneal (30 min at 400 °C), the Al/La₂O₃/Si device becomes very leaky and shows no breakdown anymore. Assuming Fowler–Nordheim tunneling through the oxide layer, the estimated energy barrier height between aluminum and La₂O₃ was 1 eV. This is 2.5 times lower than the theoretical value,¹⁰ suggesting again that the interface between aluminum and La₂O₃ is not well defined (or transformed into another material). The Weibull distributions of breakdown fields shown in Fig. 5(b) show that the breakdown is lower for the Al electrode, which is also attributed to the enhanced silicon out-diffusion in that case.

In addition, the dielectric permittivity of the La₂O₃ layer was 30% higher with TiN ($k=22.1$) than with aluminum as the top electrode ($k=17.0$). Since the interfacial silicon oxide thickness (~ 1 nm) is equal in both cases, the lower capacitance is caused by the formation of lower- k Al₂O₃ formation

at the interface ($k \sim 8.9$), which then in series lowers the total effective capacitance of the layer.

In conclusion, we have shown that significant silicon out-diffusion and aluminum in-diffusion occur in Al/La₂O₃/Si device structures even at room temperature. With TiN as the top electrode instead of aluminum, the silicon out-diffusion is suppressed considerably. This means that despite the higher cationic radii of the oxide, the presence of aluminum on top of the oxide layer largely determines the silicon out-diffusion through the high- k oxide. A TiN electrode gives lower leakage levels and improves the total device performance, whereas usage of Al as the top electrode causes aluminum in-diffusion and silicon out-diffusion, causing severe device degradation. Moreover, we conclude that atomic interdiffusion of electrode materials chosen can severely interfere with the measurement of the dielectric breakdown voltage and the reliability of an oxide.

This work has been carried out as part of the European FP6-program “REALISE” (IST-NMP 016172).

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