Enhanced electrical properties of atomic layer deposited La$_2$O$_3$ thin films with embedded ZrO$_2$ nanocrystals


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The deposition of alternating (sub)monolayers of lanthanum oxide (La$_2$O$_3$) and zirconium oxide (ZrO$_2$) by atomic layer deposition has been carried out to create uniform La$_x$Zr$_{1-x}$O$_x$ mixed oxide films. However, spontaneous nucleation of ZrO$_2$ nanocrystals occurs during deposition within an amorphous La$_2$O$_3$ matrix. Such ZrO$_2$ embedded La$_2$O$_3$ films exhibit low leakage currents in combination with higher electric breakdown fields and higher dielectric permittivities than the pure lanthanum and zirconium oxide films. The possible scenarios that account for this enhanced electric performance of these nanocluster-embedded dielectric thin films are explained. © 2008 American Institute of Physics. [DOI: 10.1063/1.3009202]

The conventional miniaturization of silicon-based microelectronic devices will soon reach the fundamental limits of atomic dimensions by 2012, as per the predictions of the International Technology Roadmap for Semiconductors. Numerous scientific and technological challenges have to be surmounted to continue Moore’s law, which predicts that the device density will double every 18 to 24 months. Since this downsizing implies further thinning of the gate oxide to a few atomic layers, tunneling of the charge carriers occurs, resulting in high leakage currents and low breakdown voltages. A solution is the application of a high-permittivity gate-oxide material that can be made thicker than silicon dioxide, which permits the same electric field across the thin film.

Numerous gate-oxide materials with high dielectric constants compared to silicon dioxide have been investigated so far. A recent comparative study on various oxides deposited with different techniques demonstrates that a relationship exists between the dielectric constant and the breakdown electric field. This empirical relation given by \( E_{BD} = \frac{20}{\kappa} \) holds for homogenous dielectric thin films, where \( E_{BD} \) is the electric breakdown field and \( \kappa \) is the dielectric constant of the material. In other words, the dielectric fails at lower electric fields with increasing \( \kappa \)-value. However, inhomogeneous layers such as nanolaminates of different dielectric materials have shown to improve the breakdown voltage.

This letter reports on nanoclustered La$_x$Zr$_{1-x}$O$_x$ films deposited by atomic layer deposition (ALD) that exhibit excellent electrical properties such as high breakdown fields, high dielectric permittivity, and low leakage currents. The possible scenarios that could explain the enhancement of electrical properties will also be discussed.

By varying the lanthanum and zirconium precursor pulse ratios, La$_x$Zr$_{1-x}$O$_x$ thin films of different compositions were deposited on p-type silicon. La:Zr pulse ratios of 1:0, 12:1, 4:1, 1:1, 1:4, 1:9, and 0:1 were used, yielding 0%, 20%, 42%, 74%, 92%, 98%, and 100% atomic Zr in the film, respectively, as measured by Rutherford back scattering (RBS) (Table I). The film thickness varied due to the different growth rates of La$_2$O$_3$ and ZrO$_2$. Details of the ALD technique and the material characterization have been reported elsewhere. After the oxide deposition, aluminum electrodes (500 nm) were sputter deposited and patterned to form rectangular metal-oxide-semiconductor (MOS) capacitors. Electrical measurements were performed on as-deposited films with an Agilent 4155C Semiconductor parameter analyzer and an HP multifrequency LCR meter on MOS structures of area ranging from 100 \( \times \) 100 to 3000 \( \times \) 3000 \( \mu \)m$^2$. A linear capacitance-area scaling was observed indicating reliable measurements. The dielectric constant of the stack was calculated using the capacitance-voltage plot in accumulation for each composition. Hence, equivalent oxide thickness (EOT) calculations include the presence of an interfacial silicon oxide layer.

Figure 1(a) depicts the dielectric constant and the leakage current through the layers as a function of the composition. Upon comparing the leakage current densities of the pure La$_2$O$_3$ or ZrO$_2$ films to the La$_x$Zr$_{1-x}$O$_x$ films, the latter exhibits more than one order of magnitude lower leakage. Considering the gradual enhancement in the dielectric constant with increasing Zr content, this reduction in leakage current seems to be counterintuitive. However, the reduction

<table>
<thead>
<tr>
<th>La:Zr pulse ratio</th>
<th>Thickness (nm)</th>
<th>Composition (% Zr)</th>
<th>EOT (nm)</th>
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<tr>
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<td>14</td>
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<tr>
<td>0:1</td>
<td>23</td>
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<td>2.99</td>
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</tbody>
</table>

*Table I. The layer thickness measured with spectroscopic ellipsometry and TEM, composition measured with RBS, and EOT as a function of the La:Zr pulse ratio.*
in leakage current density corresponds to the increase in EOT as can be seen from Fig. 1(b) where the logarithm of the leakage is plotted as a function of EOT. The La-rich films appear to have a lower leakage current than the Zr-rich films for identical EOT.

As reported earlier, the addition of Zr in La$_2$O$_3$ film causes spontaneous nanoclustering of ZrO$_2$ if the Zr content exceeds 30%. The cluster size was determined using x-ray diffraction and employing the standard Debye–Scherrer formula. It has been verified by transmission electron microscopy (TEM) that the cluster size is always two to three times smaller than the thickness of the film. Furthermore, TEM shows that the clusters are randomly distributed in the films and they do not rely on the film thickness. In Fig. 2, the variation in breakdown electric field is shown as a function of the ZrO$_2$ cluster size. Remarkably, the breakdown field increases as the zirconium content is reduced but suddenly drops when the cluster size is less than 2 nm. This sample contains 20% of Zr in the film and no significant clustering was observed here. A comparison between the empirical law and the performance of these La$_x$Zr$_{1-x}$O$_2$ films is given in Fig. 3. The average value of the films with embedded ZrO$_2$ nanocrystals is 768 ± 87, twice better than the empirical law predicts.

These enhancements in dielectric permittivity and breakdown field together with suppression of leakage current can be explained on the basis of two different scenarios. First, charges are accumulating at the interface of the dielectric with different conductivities, an effect known as Maxwell–Wagner instability. The nanocrystalline ZrO$_2$ in an amorphous La$_2$O$_3$ matrix forms multiple interfaces where charges could accumulate, creating partially charged clusters that screen the incoming electrons due to Coulomb repulsion. Similar charge trapping has been shown to occur at the interface of ZrO$_2$ particles artificially embedded in a conducting polymer matrix. Even though ZrO$_2$ is more conductive than La$_2$O$_3$ as evident from Fig. 1, the drop in leakage current in the La$_x$Zr$_{1-x}$O$_2$ films indicates that films with embedded ZrO$_2$ nanoclusters result in less conductive films than bulk ZrO$_2$. Even in Zr-rich La$_x$Zr$_{1-x}$O$_2$ films with elongated ZrO$_2$ crystals perpendicularly oriented to the surface, the leakage current remains significantly lower than in pure ZrO$_2$ films. In addition, the $k$-value becomes even larger than that of ZrO$_2$ at higher Zr concentrations. This could be due to a preferential formation of tetragonal ZrO$_2$ nanoclusters that have a higher dielectric constant than monoclinic ZrO$_2$ that coexists with the tetragonal phase in pure ZrO$_2$ films. As a consequence of the Maxwell–Wagner instability where the charges are accumulated at the dielectric interfaces, the electrical field is built up over ZrO$_2$ resulting in a larger capacitance for the total La$_x$Zr$_{1-x}$O$_2$ stack and thus a larger $k$-value.

A second scenario that accounts for the increased breakdown properties is that the percolation path for the leakage current is longer as the density of the ZrO$_2$ nanocrystals increases. Figure 4 shows an electric field simulation using a COMSOL® program, where ZrO$_2$ nanocrystals with $k=36$ are embedded in La$_2$O$_3$ ($k=27$) matrix. The results show that the electric field lines preferably propagate through La$_2$O$_3$ instead of the ZrO$_2$ clusters. The percolation path of the defects that causes the final breakdown of the film is driven by the electric field lines. This requires a higher voltage for the dielectric breakdown since the effective path length is higher than the thickness of the film. This scenario accounts for the increasing breakdown field as a function of the cluster size (Fig. 2). In the film with 20% Zr, there is no remarkable
cluster formation except for a short-range order. Hence, the breakdown is lower than for the sample with higher Zr content, where ZrO$_2$ clearly forms nanocrystals.

In conclusion, it is demonstrated that the embedded ZrO$_2$ nanocrystals in an amorphous La$_2$O$_3$ matrix significantly enhance the electrical properties of La$_y$Zr$_{1−y}$O$_x$ films. These films exhibit higher dielectric constants and high breakdown fields simultaneously, which allow an overall electrical performance of the films twice better than the limit set by the empirical law. Comparing to the conventional homogeneous dielectric thin films, these nanocluster-embedded dielectrics offer more reliable solutions for future high quality dielectrics.

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