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Enhanced electrical properties of atomic layer deposited La_2O_3 thin films with embedded ZrO_2 nanocrystals

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The deposition of alternating (sub)monolayers of lanthanum oxide (La_2O_3) and zirconium oxide (ZrO_2) by atomic layer deposition has been carried out to create uniform $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ mixed oxide films. However, spontaneous nucleation of ZrO_2 nanocrystals occurs during deposition within an amorphous La_2O_3 matrix. Such ZrO_2 embedded La_2O_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 micro-electronic devices will soon reach the fundamental limits of atomic dimensions by 2012, as per the predictions of the International Technology Roadmap for Semiconductors.¹ 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.² Since this downscaling 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.³ 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.³ 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 $E_{\text{BD}} = 20/\sqrt{k}$ holds for homogenous dielectric thin films, where E_{BD} is the electric breakdown field and k is the dielectric constant of the material.⁴ In other words, the dielectric fails at lower electric fields with increasing k -value. However, inhomogeneous layers such as nanolaminates of different dielectric materials have shown to improve the breakdown voltage.⁵

This letter reports on nanoclustered $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ 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, $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ 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_2O_3 and ZrO_2 . Details of the ALD technique and the material characterization have been reported elsewhere.⁶ 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 100×100 to $3000 \times 3000 \mu\text{m}^2$. 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_2O_3 or ZrO_2 films to the $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ 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 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.

La:Zr pulse ratio	Thickness (nm)	Composition (% Zr)	EOT (nm)
1:0	14	0	3.09
12:1	22	20	4.36
4:1	22	42	3.78
1:1	30	74	4.90
1:4	35	92	4.75
1:9	40	98	4.49
0:1	23	100	2.99

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FIG. 1. (Color online) (a) Leakage current density (J) of the samples at 1 MV/cm field. Addition of ZrO_2 in the La_2O_3 thin film causes a reduction in leakage current by one order of magnitude. The inset shows the dielectric constant of the La_2O_3 film as a function of the Zr percentage. (b) Leakage current density as a function of EOT of the films.

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,⁶ the addition of Zr in La_2O_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.⁶ 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

FIG. 2. Breakdown electric field as a function of the ZrO_2 cluster size estimated from x-ray diffraction and TEM studies (Ref. 6).

FIG. 3. Comparison between the electrical performance of the nanocluster-embedded $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ films and the empirical law where $E_{\text{BD}}^2 k = 400$ determines the "best-can-do" limit (Ref. 4).

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 $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ 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.⁷ The nanocrystalline ZrO_2 in an amorphous La_2O_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.⁸ Even though ZrO_2 is more conductive than La_2O_3 as evident from Fig. 1, the drop in leakage current in the $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ films indicates that films with embedded ZrO_2 nanoclusters result in less conductive films than bulk ZrO_2 . Even in Zr-rich $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ 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 $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ 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_2O_3 ($k=27$) matrix. The results show that the electric field lines preferably propagate through La_2O_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

FIG. 4. (Color online) Electric field lines (the dotted lines) penetrating through the oxide layer simulated for ZrO_2 nanocrystals (with $k=36$) embedded in an amorphous La_2O_3 matrix (with $k=27$) simulation. For the simulations, COMSOL® program was used.

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_2O_3 matrix significantly enhance the electrical properties of $\text{La}_y\text{Zr}_{1-y}\text{O}_x$ films. These films exhibit higher dielectric constants and high breakdown fields simultaneously, which allow an overall electrical per-

formance 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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