Dielectric investigation of high-k Y_2CuTiO_6 thin films for electronic applications

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The remarkable miniaturization trend in microelectronic industry promoted the interest in novel materials with larger dielectric constants (the so-called high-κ oxides) [1] than the conventional SiO_2, since they allow the same required capacitance value while employing a thicker gate insulator layer useful to reduce tunneling rates.

High dielectric constants have been observed in different kinds of material systems, including ferroelectric oxides [2], certain transition metal oxides and rare earth transition metal oxides [3, 4], perovskites and double-perovskites [5]. However, this search for alternatives to conventional dielectrics is complicated by the need to accept compromises in different materials. For example, HfO_2 and Ta_2O_5 have higher dielectric constants than SiO_2 (about 26 and 35 respectively) but they both suffer from high temperature coefficients and additionally HfO_2 has also much higher losses [6].

Recently with the discovery of high dielectric constant in $CaCu_3Ti_4O_{12}$ [2], transition metal oxides have become the focus of interest. In this respect, an emerging class of materials is represented by rare-earth transition metal oxides [5, 7], which belong to the Ln_2CuTiO_6 (Ln=rare earth) family. Their unusual and advantageous combination of dielectric properties, such as low dielectric loss and weak temperature and frequency dependences, beyond the high dielectric constant, make this materials a new kind of promising high-k system. However, the corresponding literature focuses so far on bulk materials while thin films with optimized properties are needed for device applications.

Among them, Y_2CuTiO_6 (YCTO) possesses a perovskite-related crystal structure and is known to crystallize in a hexagonal unit cell with space group P63cm (Figure 1a). It is a promising high-k material, according to bulk characterization data [7] demonstrating high dielectric constant (ε'=40.3) and very low losses (Tgδ=0.003) comparable to those of SiO_2 (0.001) beyond to desirable weak frequency and temperature dependences.

However the deposition and dielectric characterization of YCTO thin films have not been investigated so far. In our studies, YCTO thin films were systematically investigated and compared for the first time to SiO_2 and MgO which are commonly used dielectrics [8][9].

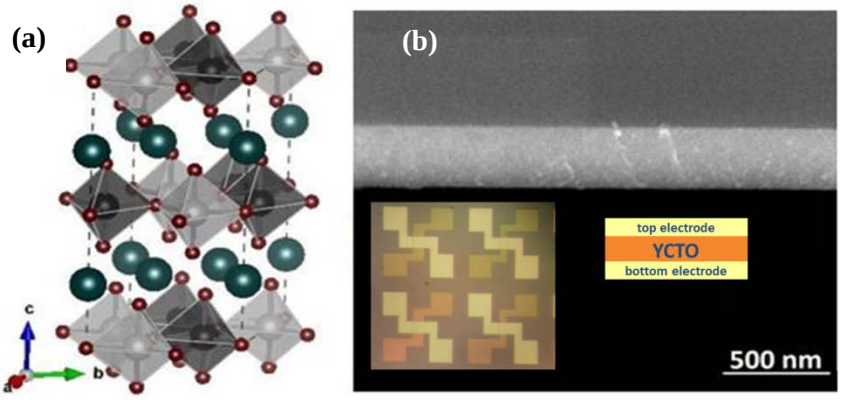

Figure 1: (a) The hexagonal unit cell of Y_2CuTiO_6; **(b)** cross sectional SEM image of a typical YCTO thin film deposited by PLD. **Inset:** electrode architecture employed for the dielectric characterization of the films deposited in arrays of parallel plate capacitors.

The YCTO thin films were deposited using Pulsed Laser Deposition (PLD) on Si/SiO_2 (5 μm) substrates with lithographed bottom electrodes, by employing a YCTO target prepared by solid states synthesis as described elsewhere [7]. PLD was chosen as deposition technique since it is able to preserve the target stoichiometry under optimized conditions. A Lambda Physics 305i ArF excimer laser (λ=193 nm, τ= 20 ns) was used with an energy density of ≈ 2J/cm^2 and a repetition rate of 10 Hz. During deposition the substrate was heated at a temperature in the range 600-650°C and the oxygen pressure was varied from 0.05 Pa to 0.5 Pa in different films, since this is expected to influence the structural and dielectric properties of these materials [10]. After deposition, films were cooled at a rate of 5°C/min while maintaining the same oxygen pressure. Au top electrodes were fabricated by standard photolithography and lift-off techniques for carrying out the dielectric measurements, by employing a cross-bar architecture (Figure 1b inset). An image of a typical YCTO film is reported in Figure 1b and shows a thickness of about 300 nm. SiO_2 and MgO thin films were also deposited in the same device architecture. In particular, SiO_2 was deposited at a rate of 1.5Å/s at 250°C using an electron beam evaporator with an oxygen flow of 10 sccm, while MgO was deposited by magnetron sputtering in Ar environment at a rate of 4 Å/min at room temperature.

For each film, 64 junctions, with different area ranging from 25 μm^2 to 90000 μm^2 were realized enabling an accurate analysis of the dielectric properties of the deposited YCTO. Special attention was dedicated to decouple the parasitic contributions from the intrinsic ones and remove the possible artefacts which can result from spurious capacitances. First, the capacitance and dissipation factor (Tgδ) for each junction were directly measured. Then, the dielectric constant $(\varepsilon'(\omega))$ was calculated at each frequency by using the film thickness and the slope resulting from the linear fit of the dependence of capacitance on the junction area accordingly to the relation, $C = \varepsilon_o \varepsilon_r \frac{A}{d}$, where ε_0 is the permittivity of free space, ε_r is the material permittivity, *A* the area of the junction and *d* the thickness of the film.

The Tgδ was calculated by the ratio of imaginary (ε'') and real part (ε') of the complex permittivity, both extracted from fitting procedure (being the conductance G=ωC*Tgδ dependent from the junction geometry and $\sigma(\omega) = \omega\varepsilon_0\varepsilon''(\omega)$). The ε' and Tgδ of the MgO and SiO_2 thin films were evaluated in a similar manner.

In Figure 2, the dielectric characterization of YCTO and MgO, SiO_2 films is reported.

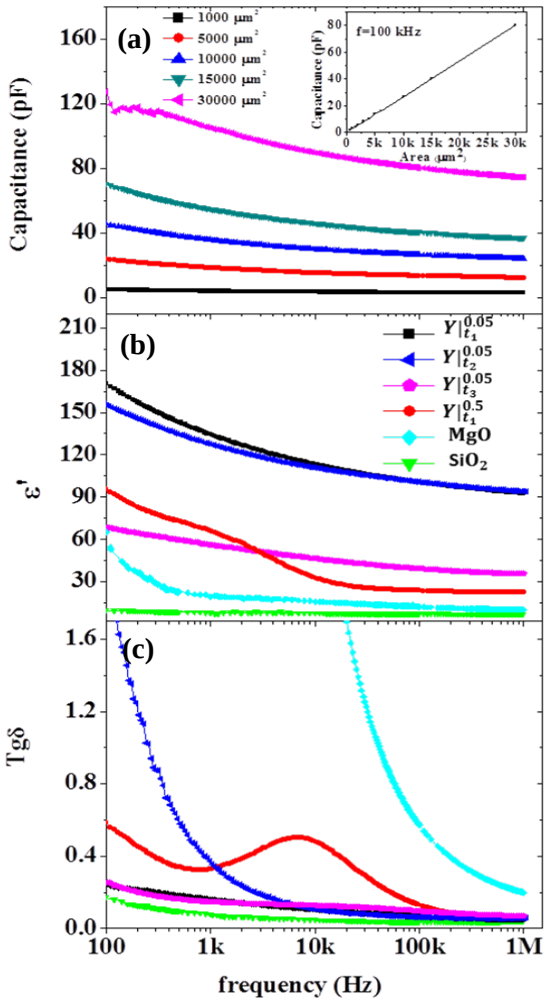

***Figure 2**: **(a)** Capacitance-frequency characteristics for capacitors having different junction areas but same YCTO thickness (300 nm) in the case of the film deposited at 0.05 Pa oxygen pressure, $\boldsymbol{Y_{t1}^{0.05}}$. **(b, c)** Comparison of dielectric constant and tangent loss among four different YCTO films ($\boldsymbol{Y_{t_1}^{0.05}}$, $\boldsymbol{Y_{t_2}^{0.05}}$, $\boldsymbol{Y_{t_3}^{0.05}}$ **and** $\boldsymbol{Y_{t_1}^{0.5}}$, where the upper index refers to the oxygen deposition pressure and the lower index to the thickness of the films, t_1=300nm, t_2=150nm and t_3=50nm) and two technologically relevant oxides: SiO_2 and MgO deposited in similar junctions.*

In particular, Figure 2a shows typical capacitance-frequency characteristics for junction areas ranging from 1000 μm^2 to 30000

μm^2 in the case of a film deposited at 0.05 Pa oxygen pressure. As expected the capacitance increases linearly with the device area (inset of Figure 2a). Figure 2b and 2c show a comparison of the ε' and Tgδ for YCTO films (at different oxygen deposition pressure and thickness), SiO_2 and MgO films. MgO and SiO_2 thin films have a ε' of 9.8 and 4 respectively at 100kHz, in good agreement with literature [11], and exhibit a negligible dependence on frequency. For all the measured frequencies, the dielectric constant of YCTO thin films is considerably higher than both the SiO_2 and MgO values. Specifically at 100 kHz, the dielectric constant of YCTO thin films deposited at 0.05 Pa ($Y_{t_1}^{0.05}$) is around 100 and it decreases to 24 in the case of thin films deposited at 0.5 Pa ($Y_{t_1}^{0.5}$). The latter film shows also a clear Debye-type relaxation that could be ascribed to a Maxwell-Wagner behaviour, indicating a variation in the film microstructure due to the different oxygen pressure. Instead a dielectric constant less sensitive to the frequency was found for $Y_{t_1}^{0.05}$ sample.

In addition by varying the thickness of the YCTO films deposited at 0.05Pa only minor changes (around 100 at 100 kHz) were observed for 300 nm to 150 nm ($Y_{t_1}^{0.05}, Y_{t_2}^{0.05}$), while a further decrease to 50 nm ($Y_{t_3}^{0.05}$) results in a relevant drop in ε', which is ≈40, approaching the values reported for the bulk counterpart.

The different dielectric response of the thinner films can be attributed to a partial oxidation of the film surface during cool down.

In conclusion we found that YCTO films resulted in superior properties than our SiO_2 and MgO thin films in similar junctions. Such experimental results further suggest that YCTO (and related materials) can have a relevant technological role for future applications since its bulk properties were found to be even improved in its thin film form by properly varying the deposition parameters.

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