Insight into the dielectric behaviour of yttrium copper titanate thin films

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Rare earth copper titanates of the Ln_2CuTiO_6 family are promising high-k materials with an unusual combination of advantageous dielectric properties, such as low dielectric loss and weak temperature and frequency dependences, beyond the high dielectric constant [1, 2]. Recently, we reported on the first detailed dielectric study on amorphous YCTO thin films [3], deposited by pulsed laser deposition on Si/SiO_2 substrates with lithographed bottom electrodes.

Figure 1 summarizes the frequency dependencies of their dielectric constant (ε') and dielectric loss (ε''). Specifically, we found a relatively high value of dielectric constant (≈100) at 100 kHz for the film deposited at 0.05 Pa ($Y|_{t_1}^{0.05}$) with only minor changes when the thickness is reduced from 300 nm ($Y|_{t_1}^{0.05}$) to 150 nm ($Y|_{t_2}^{0.05}$), while a further decrease to 50 nm ($Y|_{t_3}^{0.05}$) results in a relevant drop in ε'(≈40), as for the sample grown at a significantly larger oxygen pressure ($Y|_{t_1}^{0.5}$) with ε'=23.6. This last values approaches the permittivity reported for bulk YCTO [1, 2]. These results are technologically interesting, since they indicate that YCTO exhibits a high dielectric constant also as a thin film, with a wide tunability range driven by the deposition conditions. However, a key prerequisite for any future application is a better understanding of the physical origin of this high permittivity.

As shown in Figure 1, $Y|_{t_1}^{0.05}$ displays a typical power law frequency dependence behaviour, with both ε' and ε'' decreasing with frequency. On the other hand, $Y|_{t_1}^{0.5}$ shows a Debye-like dielectric relaxation with a smeared step in ε' accompanied by a broad peak in ε'' at intermediate frequencies. In addition, among the films deposited at 0.05 Pa, $Y|_{t_2}^{0.05}$ behaves as $Y|_{t_1}^{0.05}$, while the response of the thinnest film ($Y|_{t_3}^{0.05}$) reminds that one of the film deposited at higher oxygen pressure ($Y|_{t_1}^{0.5}$), although with a much more smeared step in ε' and a broader loss peak in ε''.

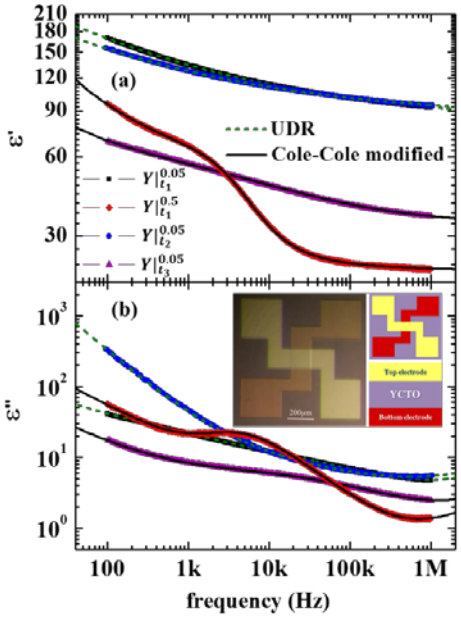

Figure 1. Frequency dependences of (a) real (ε') and (b) imaginary part (ε'') of the complex permittivity for four deposited YCTO films: $\boldsymbol{Y_{t_1}^{0.05}Y_{t_2}^{0.05}Y_{t_3}^{0.05}}$and $\boldsymbol{Y_{t_1}^{0.5}}$, where the upper index refers to the oxygen deposition pressure and the lower index to the thickness of the films, t_1=300nm, t_2=150nm and t_3=50nm). The solid (dashed) curves are the best fits to modified Cole-Cole (UDR) equations. **Inset:** Optical image and sketches of a typical MIM junction.

Both ε' and ε'' can be simultaneously fitted with appropriate dielectric dispersion models. The dielectric response of $Y|_{t_1}^{0.05}$ and $Y|_{t_2}^{0.05}$, which significantly deviate from the classical Debye behaviour, can be fitted by the UDR model [4] where the complex dielectric constant is given by:

$$\varepsilon^* = \varepsilon_\infty + A(j\omega)^{-(1-n)} \qquad (1)$$

where A is a temperature dependent parameter, ε_∞ denotes the high frequency value of dielectric constant, ω is the angular frequency and n is a parameter, typically 0.5<n<0.9 for charge-carrier dominated material system characterized by a

dielectric response showing a power law behaviour with the frequency.

However, these power-law relations are not able to describe the dielectric behaviour of the $Y|_{t_1}^{0.5}$ film in the entire frequency range, due to the downturn of ε' at intermediate frequencies and the corresponding Debye-like loss peak in ε''. This sample is characterized by a 'near Debye' dielectric response in which a loss peak is visible and the high frequency branch follows the power-law with exponent n close to zero (n≤0.1). These features highlight the departure from a pure UDR to a more general behaviour, which could be better described by the Cole-Cole equation.

To describe the Debye-type dielectric relaxation, a simple Cole-Cole relaxation equation is generally used, but in the case of $Y|_{t_1}^{0.5}$ sample, the resulting fit is not able to reproduce the entire frequency range, because the experimental low frequency dielectric dispersion is not constant. This discrepancy can be attributed to the electrical conductivity that dominates the dielectric response below 1 kHz. Thus, a modified Cole-Cole equation should be used, where the electrical conduction is taken into account as an additional term, as follows:

$$\boldsymbol{\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1+(j\omega\tau)^{1-n}} - \mathrm{j}\left[\frac{\sigma^*}{\varepsilon_0 \omega^S}\right]} \qquad (2)$$

where ε_s and ε_∞ denote, respectively, the static and high frequency values of dielectric constant, τ is the dielectric relaxation time, n is a parameter ranging between 0 and 1, which represents a measure of the deviation from the ideal Debye behaviour (n=0) and s is a dimensionless exponent (0<s<1), which for an ideal complex conductivity s=1, while s<1 indicates a distribution of carrier polarization mechanism. In the limit ω→∞, the first two terms gives the same functional form of equation 1, associated to UDR relation, which can be seen as the high-frequency asymptotic form of the Cole-Cole equation.

Table 1. Main fitting parameters. Conductivity components (σ_{DC} and σ_{SC} real and immaginary part respectively) are expressed in 10^{-10} S cm^{-1}; relaxation time (τ) in 10^{-5} s.

Sample	σ_{DC}	σ_{SC}	s	n	τ	model
$Y\|_{t_1}^{0.05}$	1.66	-	-	0.76	-	UDR
$Y\|_{t_2}^{0.05}$	169	-	-	0.78	-	UDR
$Y\|_{t_3}^{0.05}$	0.41	0.35	0.54	0.58	2.05	C-C modified
$Y\|_{t_1}^{0.5}$	2.35	0.90	0.64	0.07	3.69	C-C modified

The fits of the dielectric data of our samples are shown in Figure 1 (solid/dashed lines) and the obtained main fitting parameters are summarized in Table 1. It is important to discuss the values of the exponent n (in Table 1), since a relatively higher value of n corresponds to a more disordered system. Indeed we found that moving from a near Debye (sample $Y|_{t_1}^{0.5}$) to UDR dielectric response ($Y|_{t_1}^{0.05}$ and $Y|_{t_2}^{0.05}$ samples), the exponent value ranges from 0.07 to 0.78. It should be also observed that by increasing the exponent value, the loss peak disappears and the power-law behaviour becomes dominant. For n=0.58 (sample $Y|_{t_3}^{0.05}$) an intermediate behaviour is observed with barely visible loss peak and clear frequency-dependent relaxation. While the thicker films deposited at 0.05 Pa are characterized by similar values of n (0.76-0.78) and show a similar dielectric response, the thinner film deposited at the same oxygen pressure and the thicker one deposited at 0.5Pa are characterized by very different values of n and dielectric response. These results support a difference in film microstructure. By analyzing the imaginary part of the permittivities (ε"), it is possible to observe that, in the frequency region 100 kHz – 1 MHz, the sample $Y|_{t_1}^{0.5}$ has the lower value of ε", followed by $Y|_{t_2}^{0.05}$, $Y|_{t_1}^{0.05}$ and $Y|_{t_3}^{0.05}$. This trend can be ascribed to a higher oxygen content in the bulk of the film deposited at 0.5Pa with respect to those deposited at 0.05Pa. In addition the lower ε" value for the thinner film can be a consequence of its partial re-oxidation during cool down after thin film deposition. The different conductivity between $Y|_{t_2}^{0.05}$ and $Y|_{t_1}^{0.5}$ samples, is highlighted by the different relaxation time extracted from the fitting process (τ=2.05x10^{-5}s and 3.69x10^{-5}s for $Y|_{t_2}^{0.05}$ and $Y|_{t_1}^{0.5}$ respectively), being τ inversely proportional to the conductance of the bulk of the film.

Moreover it is widely accepted [5] that the power-law dielectric relaxation is a typical signature of the disordered matter, in which conduction takes place by hopping as a consequence of charge carriers localization due to disorder arising from amorphous structure, slight deviations from stoichiometry, doping or lattice imperfections. Considering that (i) the samples $Y|_{t_1}^{0.05}$ and $Y|_{t_2}^{0.05}$ show the dielectric features of the UDR behaviour, (ii) they could possess a mixed valence structure of Cu(I)/(II) and Ti(III)/(IV) due to the oxygen-vacancies induced by low PO_2 and (iii) they are amorphous in structure, we tentatively assign their dielectric dispersion to the charge-hopping polarization process.

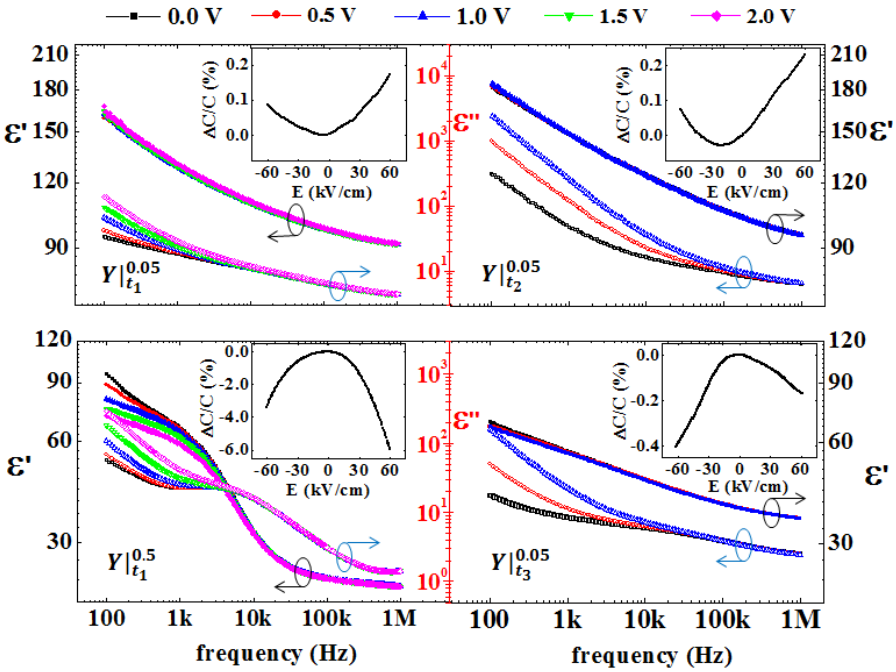

Figura 2. Capacitance as a function of the frequency at different fixed DC bias values: 0V (black), 0.5V (red), 1V (blue), 1.5V (green) and 2V (magenta), with filled and empty points corresponding to ε' and ε'' respectively. Inset: Percentage variation of the capacitance as a function of the electric field measured at 1 kHz showing a Schottky response for samples $Y|_{t_1}^{0.5}$ and $Y|_{t_3}^{0.05}$ while in the other samples an increase is observed which can be associated to the presence of traps.

At this point, the last issue to explore regards the understanding of the origin of the permittivity drop and the loss peak at intermediate frequency in $Y|_{t_1}^{0.5}$ and $Y|_{t_3}^{0.05}$. Figure 2 shows the permittivity-frequency $(\varepsilon' - f)$ curves of the YCTO capacitors measured by applying an additional DC bias beyond the measuring AC voltage. The dielectric constant remains almost voltage independent in $Y|_{t_1}^{0.05}$ and $Y|_{t_2}^{0.05}$ samples, while it decreases with increasing bias voltage in the low frequency range in $Y|_{t_1}^{0.5}$ and $Y|_{t_3}^{0.05}$ samples, most significantly in the first one. In $Y|_{t_1}^{0.5}$ and $Y|_{t_3}^{0.05}$ samples the low frequency (from 100Hz to 10kHz) dielectric response could be ascribed to top and bottom interfaces, while the high frequency response without evident voltage dependence corresponds to the bulk of the films. This suggest also that $Y|_{t_1}^{0.05}$ and $Y|_{t_2}^{0.05}$ films are characterized by a bulk dominated response in the whole frequency range. In samples $Y|_{t_1}^{0.5}$ and $Y|_{t_3}^{0.05}$, the observed decrease in permittivity with increasing frequency (following a Debye-like relaxation) and the voltage dependent capacitance (following the Schottky relation, see the percentage capacitance variation ΔC/C (%) reported in the insets of Figure 2) can be attributed to the Maxwell-Wagner interfacial polarization effect [6] due to the presence of electrical heterogeneous regions in the film. As far as applications are concerned, our study demonstrates that YCTO thin films exhibit a high dielectric constant widely tunable by acting on the deposition conditions. In this regard, the thinnest film being characterized by (i) low conductivity in all the frequency range investigated, (ii) a less pronounced loss peak and a relatively high dielectric constant, is very promising as high-k gate oxide.

Acknowledgements

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