Scanning Probe Microscopy on heterogeneous CaCu$_3$Ti$_4$O$_{12}$ thin films

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Abstract
The conductive atomic force microscopy provided a local characterization of the dielectric heterogeneities in CaCu$_3$Ti$_4$O$_{12}$ (CCTO) thin films deposited by MOCVD on IrO$_2$ bottom electrode. In particular, both techniques have been employed to clarify the role of the inter- and sub-granular features in terms of conductive and insulating regions. The microstructure and the dielectric properties of CCTO thin films have been studied and the evidence of internal barriers in CCTO thin films has been provided. The role of internal barriers and the possible explanation for the extrinsic origin of the giant dielectric response in CCTO has been evaluated.

I. Introduction
The electrical properties of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) ceramics and single crystals received considerable attention due to the effective huge permittivity (up to $10^5$) measured in the radio frequencies range, furthermore stable in the 100-400 K temperature range [1-3]. In the recent literature, this giant permittivity has been commonly related to extrinsic effects, i.e. not associated to the bulk material property itself. Possible extrinsic mechanisms to account for the colossal permittivity behaviour have been supported by results from impedance spectroscopy (IS) [4], Raman spectroscopy [5] and first-principles calculations [6]. In particular, the IS data on CCTO polycrystalline ceramics reported so far, have been modelled considering an equivalent circuit of two elements, each consisting of a parallel resistor-capacitor (RC), connected in series. One RC element ($R_{gb}$ and $C_{gb}$) simulates the grain boundary response, whereas the other ($R_{b}$ and $C_{b}$) simulates the bulk contribution [4]. The model is suitable to simulate, in a first approximation, the measured capacitance (C) vs. frequency (f) curves showing relaxation at high frequencies. Therefore, the origin of the huge permittivity, arising from the capacitive response before the observed relaxation, has been mainly attributed to an internal barrier layer capacitor (IBLC) behaviour associated with insulating grain boundaries and semiconducting grains structure. This explanation has been corroborated imaging the insulating barriers at the grain boundaries of CCTO ceramics by both nanocontact current-voltage measurements [7] and Scanning Probe Microscopy (SPM) with conductive tips [8,9] as already demonstrated on other microelectronic investigation [10,11].

However, for microelectronics applications, CCTO thin films are much more interesting than ceramics, thus for those applications the occurrence and the origin of the high permittivity deserve to be reliable demonstrated and studied specifically in thin films. In this context, it should be noted that the IBLC model cannot be responsible for the giant permittivity observed in CCTO single crystals [12] as well as in epitaxial columnar thin films [13], where no grain boundary is crossed between the two planar electrodes parallel to the surface. In fact, the giant response, indeed observed nowadays in thin films, has been explained considering an electrode effect according to the Maxwell-Wagner (MW) model [14], and this raises the question, to date not definitively studied and discussed, about the CCTO capacitor reliability and the importance of Schottky barriers at the electrode-surface interfaces [15].

In this paper, we report on CCTO thin films deposited by Metal-Organic Chemical Vapor Deposition (MOCVD) possessing a “bricks wall” (BW) morphology and a giant permittivity. In this case the IBLC effect can be present. Here, we demonstrate its occurrence and we evaluate the necessary conditions for a reproducible achievement of huge capacitive density in CCTO integrated condensers.
II. Experimental

CCTO films have been deposited by a two-steps MOCVD processes on IrO$_2$/Ir/TiO$_2$/SiO$_2$/Si substrate using the condition parameters described elsewhere and 180 minutes deposition time [16-18].

The electrical characterization at nanometre scale was performed by a VEECO D3100 atomic force microscope (AFM) equipped with a Nanoscope V controller and the Nanoman head operating in air, in contact mode and in closed loop condition, using the Conductive Atomic Force Microscopy (C-AFM) module. Standard experiments were carried out using Nanoworld boron doped diamond tips [19-22]. Laser off measurements have been also carried out to exclude the influence of the laser on the reported electrical measurements at nanoscale.

The macroscopic capacitances versus frequency (C-f) measurements were carried out on Pt/CCTO/IrO$_2$ capacitors by adopting the Terman method and using a HP 4284A equipment at an AC voltage with a fixed amplitude of 50 mV. The test devices have been fabricated with top electrodes having an area of $10^4$ $\mu$m$^2$ obtained by a photolithographic lift-off process of the sputtered platinum layer.

The macroscopic characteristics were collected at different temperatures, in a range from 298 to 473 K.

III. Results

Several papers reported on CCTO thin films grown by PLD (Pulsed Laser Deposition) or others physical methodologies presenting columnar morphologies (Figure 1a) where no barriers parallel to the electrodes are present similarly to single crystal [23,24]. Our CCTO thin films have been grown on IrO$_2$/Ir/TiO$_2$/SiO$_2$/Si substrate by MOCVD, a more industrial friendly technique. They are polycrystalline with rounded grains about 100 nm wide. The film morphology is similar to that observed in ceramics, called “bricks wall” (BW) morphology, and is characterized by many grain boundaries parallel to the electrode surface (Figure 1b) in contrast with the typical columnar growth (Figure 1a) observed in CCTO films deposited by PLD.

Capacitance vs. frequency (C-f) curves have been measured in the $10^2$-$10^6$ Hz range and at different temperatures from 298 up to 473 K. Typical capacitance versus frequency curves (Figure 2) have been collected at several temperatures and both point out to a peculiar temperature dependent relaxation behaviour: the relaxation frequency increases upon increasing temperature. This trend, observed by macroscopic measurements, is similar to that found in CCTO ceramics, thus it could be also interesting the comparison of the dielectric behaviours at nanoscale.

The nanoscale mapping of the electrical response is reported in Figure 3 at room temperature. It was carried out in order to distinguish the presence of an internal barrier [25] or a superficial polarization [26]. The current map (a) has been collected on the bare CCTO thin film surface. Insulating grain boundaries and conducting grains are clearly visible (Figure 3a). This dielectric structure recalls the CCTO ceramics considering also the BW morphology. Further details have been provided by the current versus voltage (I-V) curves, locally collected by C-AFM on a 10x10 matrix points, each spaced of 200 nm. The I-V curves clearly belong to two families as reported in the related histogram (Figure 3b). The first family is centred at high current values and the second at quite lower current values. They can be
respectively related to the current flowing through the
grain (when the tip is statistically contacting a grain) or
the grain boundaries (when the tip is occasionally con-
tacting the grain boundaries). The current flowing
through the grain boundaries is at least two orders of
magnitude lower than in the grains as already observed
in CCTO polycrystalline ceramics [27].

The present CCTO films possess a BW structure with
conducting grains surrounded by insulating grain
boundaries, thus prompting to consider the IBLC model
as a possible explanation for the observed temperature
dependence of the relaxation frequencies.

IV. Discussion
Previous reports [26,27] have shown that the micro-
structure and the electrical properties of CCTO cer-
amics are strongly dependent on processing conditions.
In fact, the grain size increases with increasing the sin-
tering temperature and/or the processing time as well
[26,27]. The presence of the IBLC effect on CCTO cer-
amics has been also reported and related to the synthesis
conditions.

The fabrication of “bricks wall” CCTO thin films
encourages the analogy with the ceramics (not possible
for columnar films). Both the presence of a temperature
relaxation frequency dependence (Figure 2a) and the
presence of insulating grain boundaries surrounding
semiconducting grains (Figure 3a) urges the use of the
IBLC model to explain the giant permittivity response in
thin films.

Considering now the dielectric characteristics (Figure 2)
when the IBLC is present, the temperature dependent
relaxation frequency can be used to study the electrical
properties of the grain boundaries. Their barrier height
can be determined by measuring the current flowing in a
wide temperature range (298-473 K). In fact, the presence
of internal barriers can be related to a hopping transport
model inducing a thermal activated conductivity [7]. The
Arrhenius plot of the measured conductivity allowed to
estimate the grain boundary barrier activation energy, it
is $E_a \sim 0.25$ eV. This measured activation energy for the
conduction in the CCTO films is lower than found in
ceramics [26,27]; this discrepancy can be essentially
explained by the different conducting/insulator volume
fraction in the two cases due to the huge difference
in the grain size.

Finally, it is noteworthy that remarkable high capaci-
tance density (about 100 nF/mm²) can be achieved at
room temperature with a reasonable dispersion factor
($\tan \delta < 1$ at 1 MHz) and in a wide frequency range
($10^2$-$10^6$ Hz) at 473 K.

V. Conclusion
CCTO thin films presenting a BW structure have been
fabricated by MOCVD. In these films the main mechan-
ism has been proposed for the explanation of the extrin-
sic giant permittivity response. The presence of the
IBLC effect was demonstrated. Remarkable high capaci-
tance density (about 100 nF/mm²) can be achieved at
room temperature.

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Authors’ contributions
PF carried out the electrical characterization and conceived of the study. RL
performed the film deposition and conceived of the study. VR conceived of
the study and participated in its design and coordination section. All authors
read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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