

CaCu₃Ti₄O₁₂ thin films for capacitive applications:
MOCVD synthesis and nanoscopic/microscopic
characterization

Raffaella Lo Nigro,^{a*} Roberta G. Toro,^b Maria Rita
Catalano,^b Graziella Malandrino,^b Ignazio L. Fragalà,^b
Patrick Fiorenza^a and Vito Raineri^a

^aIMM, sezione di Catania, CNR, Strada VIII n 5, 95121
Catania, Italy.

raffaella.lonigro@imm.cnr.it

^bDipartimento di Scienze Chimiche, Università di
Catania, and INSTM, UdR Catania, Viale A. Doria 6,
95125 Catania, Italy.

The increasing need to miniaturize capacitor devices is demanding for progressively higher dielectric constant materials. Recent studies have demonstrated that the calcium copper titanate, CaCu₃Ti₄O₁₂ (CCTO), single crystals and ceramics possess impressive dielectric constant values of about 10⁵ working at 1 MHz which remain constant in the 100-600K temperature range and slightly depend upon work frequency in the 10²-10⁵ Hz range.¹⁻³ Fabrication of thin films becomes now a required issue to understand their properties and evaluate potentialities for device integration.

The synthesis of a multi-element oxide phase often requires considerable efforts to define the appropriate deposition conditions for the fabrication of high quality thin films and in particular the MOCVD growth process depends critically on the availability of volatile, thermally stable precursors. CaCu₃Ti₄O₁₂ (CCTO) thin films have been successfully deposited on LaAlO₃ (100) single substrates and on Pt/TiO₂/SiO₂/Si(100) stacks using Metal Organic Chemical Vapor Deposition technique, a suitable method even for large-scale production. A novel approach based on a molten multi-component precursor source has been applied. The molten mixture consists of the Ca(hfa)₂•tetraglyme, Ti(tmhd)₂(*i*-Opr)₂, and Cu(tmhd)₂ [Hhfa= 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; tetraglyme= 2,5,8,11,14-pentaoxapentadecane; Htmhd= 2,2,6,6-tetramethyl-3,5-heptandione; *i*-Opr = iso-propoxide] precursors.⁶⁻⁸

Film complete structural and morphological characterizations have been carried out by several techniques [X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM)]. The in-situ deposited CCTO (001) films on LaAlO₃ (001) substrates are of high quality as evidenced by their in-plane and out-of-plane alignments investigated using X-ray and electron transmission diffraction patterns. CCTO films grown on Pt/TiO₂/SiO₂/Si(100) industrial substrates are polycrystalline (Figure 1) and present more disordered morphologies (Figure 2).

Moreover, the electrical characterization at micro (Figure 2) and nanometer scale has been performed. The permittivity imaging provided at nanometer scale by Scanning Impedance Microscopy provided a correlation between the physical properties and structural characteristics. The nano impedance modulus and phase have been detected and the permittivity of the single CCTO layer has been calculated to be about 8000 at 90 kHz.⁹

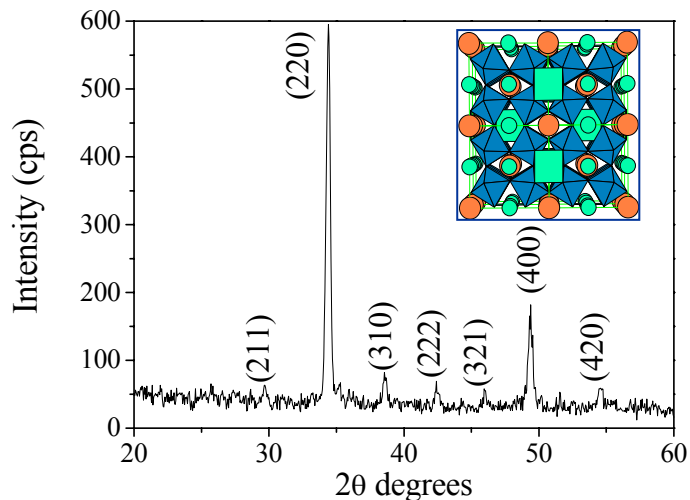


Figure 1. XRD of CCTO polycrystalline films on Pt electrode and CCTO unit cell as inset.

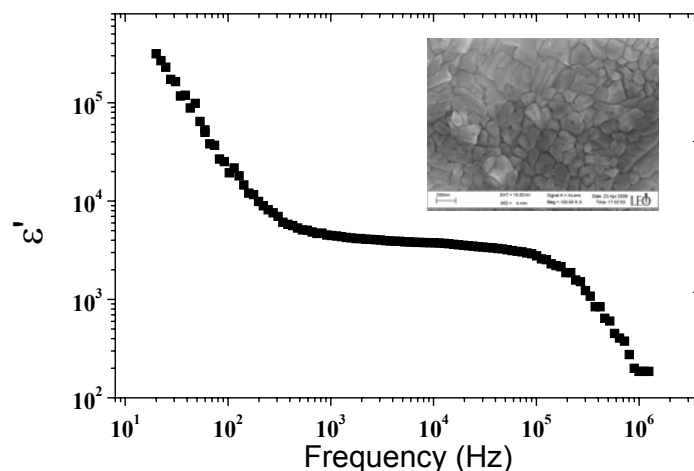


Figure 2. Dielectric constant values in function of frequency of CCTO polycrystalline films on Pt electrode and their morphology as inset.

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