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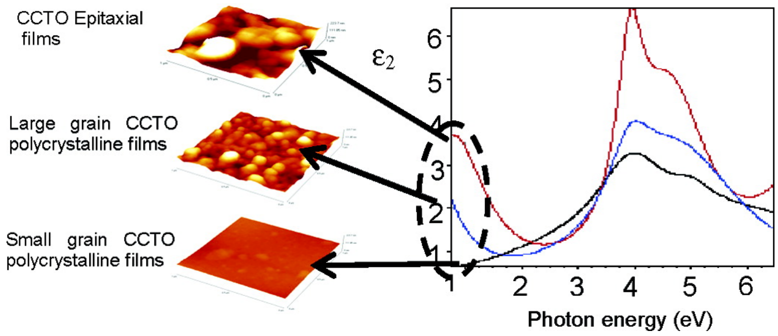

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Recent Advances in Characterization of $CaCu_3Ti_4O_{12}$ Thin Films by Spectroscopic Ellipsometric Metrology

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The increasing need to miniaturize capacitor devices is demanding for progressively higher dielectric constant materials. In this context, recent pioneering studies have shown that the perovskite related calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO), possesses an impressive dielectric constant (ϵ) value of 10^5 at 1 MHz without suffering from limitations of commonly used ferroelectric materials. In addition, this material does not show ferroelectric transition in a wide 100−600 K temperature range, where the ϵ value remains constant.[1−3] In this perspective of technological relevance, intriguing basic questions, involving the nature and origin of large dielectric constant values, remain almost unsolved. In particular, it is a debated aspect whether the dielectric behavior relies upon a response which is intrinsic to a perfect CCTO crystal or, on the contrary, upon an extrinsic origin due to defects and/or inhomogeneities.[4,5] It, therefore, becomes of great importance to grow thin films in order to study their intrinsic dielectric properties. To date, CCTO films have been fabricated by pulsed laser deposition,[6−9] while recently, we have developed the CCTO thin film growth on $LaAlO_3(100)$ substrates by a novel MOCVD approach[10] that is more compatible with a large-scale production. In this paper, we report the first synthesis of CCTO films on technologically important substrates unfolding the electronic dielectric functions of different nanostructured CCTO films by spectroscopic ellipsometry. Present data develop a robust link between the dielectric functions, $\epsilon(\omega)$, and the nanostructures of the CCTO films deposited under various conditions.

The present and up to date "unique" MOCVD process for the fabrication of CCTO thin films relies upon a novel approach which is based on the use of a molten multicomponent precursor source consisting of a homogeneous mixture of $Ca(hfa)_2$•tetraglyme, $Cu(tmhd)_2$, and $Ti(tmhd)_2(i\text{-}Opr)_2$ [Htmhd = 2,2,6,6-tetramethyl-3,5-heptandione; *i*-Opr = isopropoxide; Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, tetraglyme = 2,5,8,11,14-pentaoxapentadecane] in a 1:1:3 stoichiometric ratio. CCTO films have been grown on $LaAlO_3(100)$ and $Pt/TiO_2/SiO_2/Si(100)$ substrates through a two-step in situ MOCVD process. Thus, the Ca−Cu−Ti oxide matrix deposition has been carried out at 600 °C in the ~3−4 Torr range, while variations of conditions of the following annealing step result in three differently structured CCTO films. In particular, epitaxial (001)CCTO films form on $LaAlO_3$ by annealing at 760 Torr in O_2 atmosphere at 900 °C for 120 min. Samples grown on $Pt/TiO_2/SiO_2/Si(100)$ substrates and in situ annealed at 750 °C either for 240 or for 30 min form random CCTO films.

The CCTO film deposition on $LaAlO_3$ substrate has been the leading step for the CCTO growth process optimization since $LaAlO_3$ substrate, for its stability at high temperatures, presents less stringent requirements. Moreover, the perovskite nature, as well as the small lattice mismatch (~2.5%), drives the epitaxial growth of the CCTO films. The present synthesis of pure CCTO films on $Pt/TiO_2/SiO_2/Si(100)$ technological substrates represents a real improvement on the route to their commercial implementation.

The structural characterization of the present epitaxial CCTO films on $LaAlO_3$ perfectly matches earlier reported data,[10] while the X-ray diffraction (XRD) patterns on Pt substrates (Figure 1) of both films annealed at 240 and 30 min are closely comparable and point to the formation of polycrystalline CCTO films.

Remarkably different morphologies are evident in the atomic force microscopy (AFM) images (Figure 2a−c). Epitaxial CCTO films on $LaAlO_3$ substrates possess 200−300 nm wide grains, while polycrystalline CCTO films deposited on Pt substrates show smaller grains of about 100 and 50 nm in the case of 240 and 30 min annealings, respectively. Of course, the observed differences depend on the used annealing temperatures and, in the case of CCTO samples deposited on Pt substrates, on the duration of the annealing process. Grain boundaries in CCTO films crucially control dielectric properties due to their impact on the values of density and polarizability, which, in turn, are related to the dielectric constant through the Clausius−Mosotti equation. Therefore, the most intriguing issue associated with the present data is related to the different ratios between grain areas and grain boundary areas in each class of CCTO films.

Despite the fact that electrical properties of CCTO films have been largely investigated,[6−8] their optical properties and their dependence on film microstructure remain scarcely addressed. Thus, few reports exist on the reflectivity in the far-infrared energy range.[9] The present investigation provides the first data on the optical response of CCTO films from the near-infrared to the ultraviolet using spectroscopic ellipsometry in the photon energy range of 0.75−6.5 eV.

Optical properties are determined by free carriers and interband electronic transitions.[11] The band modifications due to electronic transitions contain information on film microstructures and consist of changes of shape and position of dielectric function features. It is, therefore, evident that a correlation between optical functions and film structure can be established. Figure 3 shows the spectra of the real, ϵ_1 ($= n^2 - k^2$), and imaginary, ϵ_2 ($= 2nk$) (where n is the refractive index and k is the extinction coefficient), parts of dielectric functions for epitaxial and polycrystalline CCTO films. The spectra have been corrected for any roughness effect by using in the ellipsometric analysis the substrate/film/surface roughness model. Electronic transitions to unoccupied conduction band states, which are primarily Ti 3d-like (mainly t_{2g} states), are responsible

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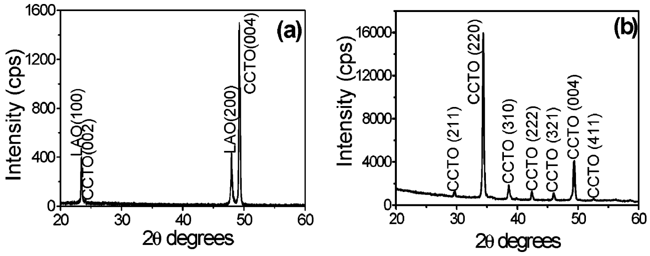

Figure 1. (a) X-ray diffraction patterns of CCTO films deposited on $LaAlO_3(100)$ substrate (a) and on Pt substrate (b).

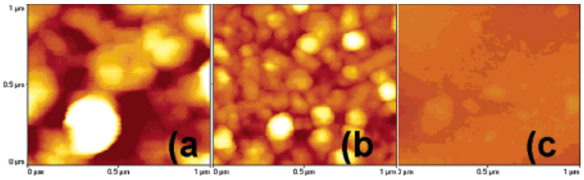

Figure 2. AFM images (1 μm × 1 μm) of the CCTO films grown on (a) $LaAlO_3(100)$ substrate at 900 °C for 120 min; (b) Pt substrate at 750 °C for 240 min; and (c) Pt substrate at 750 °C for 30 min.

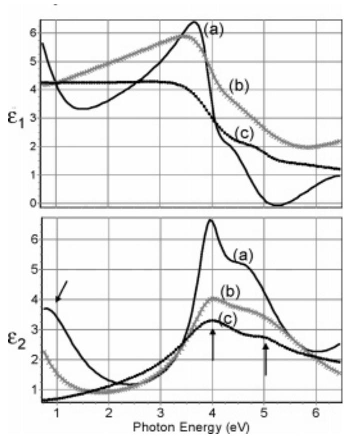

Figure 3. Spectra of the real part, ϵ_1, and of the imaginary part, ϵ_2, of the dielectric functions of CCTO films with different grain size annealed on (a) $LaAlO_3$ at 900 °C for 120 min and on (b−c) the $Pt/TiO_2/SiO_2/Si(100)$ substrate at 750 °C for 240 and 30 min, respectively.

for the peaks observed in the ϵ_2 spectrum at approximately 4 eV, while e_g states are represented by the peaks at approximately 5 eV.[12] The greater amplitude of ϵ_2 in this range and the higher dispersion in spectra of the refractive index correlate with the better structural order of both epitaxial films and polycrystalline films with larger grain size. This is a well-known effect largely described in the literature for poly- and microcrystalline silicon.[13]

Another major difference in the ϵ_2 spectra has been observed for photon energies below 2 eV. This feature cannot be related to electronic transitions, otherwise it should have been observed in all the three samples. Nevertheless, free carrier absorption might occur in this energy range, as shown for epitaxial and large grain polycrystalline films. This observation suggests that these films consist of semiconducting grains separated by insulating grain boundaries. As in many semiconductor oxides, the semiconducting character is related to oxygen vacancies. The oxygen vacancies and free charges (electrons) within the semiconducting grain might be generated during the annealing treatment that causes the transition from amorphous to crystalline films. Although annealing is performed in oxygen atmosphere, compensation of grain boundaries that increases their insulating character might occur, while the grain core keeps its O vacancies since grain boundaries act as a sink-site for oxygen. Therefore, the formation of grains accompanies generation of free electrons in the grain core, which give rise to the low-energy absorption.

The observation in the optical spectra of a distinctive and easy-to-monitor feature sensitive to oxygen vacancies represents a great issue since oxygen has a strong impact on the value of the dielectric constant. Compensation of oxygen vacancies (optically readable in the absence of the low-energy absorption in ϵ_2) causes the decrease of the dielectric constant.[4,5] Therefore, optical spectra and amplitude of optical transitions can be used to relate film structures to optical and electrical CCTO properties. In particular, the free carrier absorption (indication of the oxygen vacancies) and the higher amplitude of the dielectric function (through the Clausius−Mosotti equation) represent reliable indicators of a qualitative trend of the dielectric constant of films, namely, the higher the dielectric function spectra, the greater the dielectric constant. In this specific case, ϵ_∞ values of 1.6 and 1 are observed, respectively, for the epitaxial and polycrystalline films. Note that ϵ_∞ only accounts for the electronic contribution and relates to a frequency of about 10^{13} Hz, while the giant dielectric value measured at 10^3 Hz also includes the ionic contribution and dipolar polarizability.

To our knowledge, this represents the first report of an MOCVD in situ process for the fabrication of giant dielectric constant CCTO films on a technologically important substrate. These results, as a whole, represent a doubtless step ahead in the perspective of industrial production, and the ellipsometric studies themselves have filled the gap in the knowledge of the optical properties in the near-infrared/visible/near-UV spectral energy range. Finally, and even more interesting, ellipsometric characterization represents a non-destructive tool for film functional characterization, and therefore, it has to be considered as an appealing method for characterization of large-area products during the manufacturing cycle processes.

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Supporting Information Available: Details of deposition process and film characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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