Effects of postanneal conditions on the dielectric properties of $CaCu_3Ti_4O_{12}$ thin films prepared on $Pt/Ti/SiO_2/Si$ substrates

Liang Fang[a] and Mingrong Shen
Department of Physics, Suzhou University, Suzhou 215006, People's Republic of China

Wenwu Cao[b]
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

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High-dielectric-constant $CaCu_3Ti_4O_{12}$ (CCTO) thin films were prepared on $Pt/Ti/SiO_2/Si(100)$ substrates by pulsed-laser deposition (PLD). The 480 nm thick polycrystalline films have preferred orientation and show obvious crystallization on the surface. The temperature dependence of dielectric constant and loss of the Pt/CCTO/Pt capacitors is comparable with that obtained in the epitaxial CCTO films grown on oxides substrates. We found that the dielectric properties are very sensitive to the postannealing atmosphere and temperature. Postannealing in nitrogen atmosphere produces larger low-frequency dielectric relaxation as the annealing temperature increases, while annealing in oxygen atmosphere at high temperature suppresses the relaxation and decreases the dielectric constant of the thin films. Such results are attributed to the presence of insulating grain-boundary barrier layers. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1728308]

With the trend of size reduction of many microelectronic devices, high-dielectric-constant oxides have become increasingly important in microelectronics. Recently, much attention has been paid to an unusual cubic perovskite material $CaCu_3Ti_4O_{12}$ (CCTO).[1–11] Both single crystal and ceramic of CCTO have very high dielectric constant (of the order of 10^4) at room temperature and remains almost constant in the temperature range from 100 K to 600 K. Moreover, from neutron powder diffraction[2] and high resolution x-ray diffraction,[3] no evidence of any structural phase transition was found in CCTO from 100 K to 600 K, which is very desirable for practical device applications.[1]

Some groups have successfully grown high-quality epitaxial CCTO films on oxide substrates.[12,13] These films show single-crystal structure and the dielectric constants are larger than 1500 in a wide temperature range. This investigation concentrates on CCTO thin films deposited directly onto Si substrates. Such films could be used in practical large-scale integrated circuits since they are compatible with semiconductor technology. In addition, we will study the effects of postannealing in different atmosphere and at different temperatures on the dielectric properties.

CCTO pellets used as PLD targets were prepared by mixed oxide method. High purity $CaCO_3$, TiO_2, and CuO powders were weighted in appropriate ratio, mixed by ball milling for 10–16 h, calcined at 750 °C for 2 h, and then pressed into pellets. The pellets were finally fired at 1100 °C for 2 h. CCTO thin films with 480 nm in thickness were made on $Pt/Ti/SiO_2/Si(100)$ substrates by the PLD technique.[14] A 248 nm KrF excimer laser (Lambda Physik 105i) operated at 5 Hz was focused on a high-density ceramic target of CCTO with an energy density of 2 $J\,cm^{-2}$. The chamber was firstly pumped down to 2×10^{-6} Torr, then oxygen was introduced to a pressure of 200 mTorr. The substrate was heated to 720 °C by a resistance heater during deposition. Using radio frequency (rf) sputtering technique, Pt electrodes with a diameter of 0.28 mm were deposited onto the top surface of the films at room temperature through a shadow mask. After deposition of the top electrodes, the samples were given different postanneal treatments in a tube furnace. The temperature dependence of the dielectric properties was measured by a HP4284 LCR meter from 100 K to 350 K in a Delta 9023 oven. The frequency dependence of the dielectric properties was measured using a HP4294A impedance analyzer over a frequency range of 100 Hz to 2 MHz.

Figure 1 shows the x-ray diffraction (XRD) patterns of the CCTO target and the CCTO thin film on $Pt/Ti/SiO_2/Si(100)$ substrates by a Rigaku D/MAX 3C XRD diffractometer using Cu $K\alpha$ radiation at 40 kV. It can be seen that (211), (220), (400), and (422) peaks match the characteristics of the CCTO compounds, demonstrating a polycrystalline characteristics. In addition, compared with the target, the ratio $I(220)/I(422)$ is higher in the film, indicating a (220) preferential orientation for the CCTO thin film on $Pt/Ti/SiO_2/Si$ substrates.

The surface morphology of the CCTO film was analyzed by a Hitachi S-5750 SEM, as shown in the inset of Fig. 2(a). The film surface is crack-free and quite smooth. There are many square shaped grains stacking onto each other showing on the film surface, which is consistent with the XRD result indicating (220) preferential orientation. The cross-sectional SEM morphology is presented in the inset of Fig. 2(b). The dense CCTO thin films grow columnlike, and the interface between the CCTO film and Pt electrode was clean and

[a]Author to whom correspondence should be addressed. Electronic mail: lfang@suda.edu.cn
[b]On leave from the Pennsylvania State University.

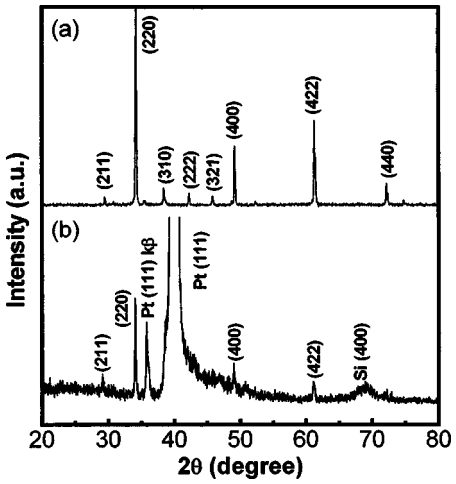

FIG. 1. X-ray diffraction patterns of the (a) CCTO target and (b) CCTO thin film.

sharp, which implies negligible interdiffusion across the interface.

The temperature dependence of the dielectric constant $\varepsilon(T)$ and the loss tangent $\tan\delta(T)$ under different frequency for the as-deposited Pt/CCTO/Pt capacitors is shown in Figs. 2(a) and 2(b), respectively. The dielectric constant has a fairly high value of about 2000 and the loss tangent is less than 0.5 at room temperature below 10 kHz and show obvious frequency dispersion. The dielectric constant decreases rapidly with decreasing temperature in the low temperature region [this drop in $\varepsilon(T)$ below 10 kHz is not shown here due to the limited temperature range of our measurements]. Moreover, there is a broad peak in $\tan\delta(T)$ at 1 MHz corresponding to the sharp drop of $\varepsilon(T)$, and the temperature peak of the dissipation shifts to lower temperatures with the decrease of frequency. The dielectric constant and loss tangent as well as the characteristics of their temperature dependence at different frequencies are comparable with those obtained in the epitaxial CCTO films grown on oxides substrates.[13]

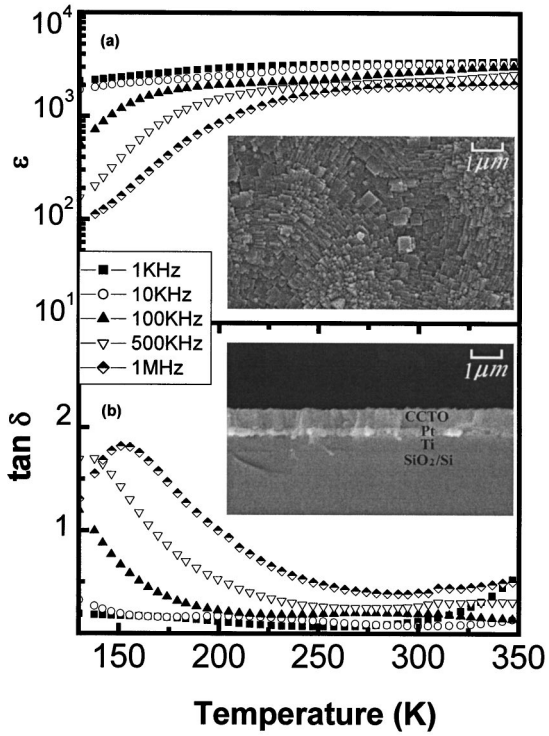

FIG. 2. The temperature dependence of (a) the dielectric constant ε and (b) the loss tan δ for the CCTO films at different frequencies. The surface morphology of the CCTO thin film was inserted in Fig. 2(a) and the cross-section morphology of the CCTO thin film was inserted in Fig. 2(b).

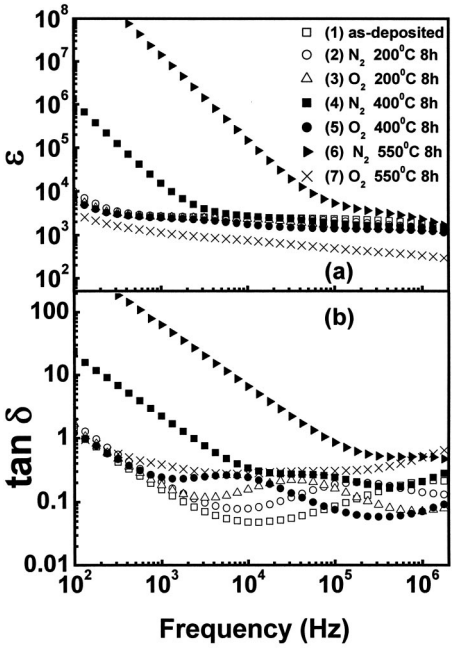

FIG. 3. Frequency dependence of the dielectric constant ε (a) and the loss tan δ (b) for (1) as-deposited Pt/CCTO/Pt capacitors, (2) postannealed in nitrogen at 200 °C, (3) postannealed in oxygen at 200 °C, (4) postannealed in nitrogen at 400 °C, (5) postannealed in oxygen at 400 °C, (6) postannealed in nitrogen at 550 °C, and (7) postannealed in oxygen at 550 °C.

Figures 3(a) and 3(b) shows the variations of the dielectric constant and loss tangent as a function of frequency for the as-deposited Pt/CCTO/Pt capacitors and the same film after annealing in O_2 or N_2 atmospheres at different temperatures. Note the as-deposited capacitors have gone through six different postannealing processes as illustrated in Fig. 3. Low temperature annealing at 200 °C in nitrogen and oxygen shows no significant changes in the dielectric properties. However, very large dielectric relaxation in low frequency region (below 3 kHz) appeared when the sample was postannealed at 400 °C in N_2. This relaxation effect disappeared when a subsequent postannealing was performed in O_2 at the same temperature. Larger dielectric relaxation, both for dielectric constant and loss tangent, was observed when the sample was postannealed at 550 °C in N_2 atmosphere. Again, the relaxation phenomenon disappeared after the sample was exposed to O_2 at 550 °C for 8 h. It appears that annealings in N_2 and O_2 atmosphere produce countereffects. One must note that the dielectric constant decreased substantially after this N_2 and O_2 atmosphere annealing cycle. Using XRD and scanning electron microscopy, we found no structural changes for the samples experienced all the above postannealing processes.

The mechanism behind the high dielectric constant of the CCTO ceramics and crystals has been studied by several groups.[1–4,8,10] Recently, the study on impedance spectroscopy[6,11] demonstrated that the CCTO ceramics are composed of semiconducting grains separated by insulating grain boundaries. The origin of the semiconductivity in the grains may arise from a small but countable amount of oxygen loss during the ceramic fabrication. High-dielectric-constant phenomenon is thus attributed to the grain-boundary mechanism, as found in internal barrier layer capacitors.[15] The same mechanism is used to explain the high-dielectric-constant phenomenon in Li and Ti doped NiO.[16] The CCTO films in the present study are polycrystalline and composed of many grains, as illustrated in Figs. 1 and 2. The postannealing effects on the dielectric properties are very similar to those happened in the ferroelectric polycrystalline film capacitors, such as $Pt/BaSrTiO_3/Pt$ capacitors.[17,18] Therefore, we proposed that the present CCTO films on $Pt/Ti/SiO_2/Si$ substrate are also composed of semiconducting grains and insulating grain boundary. When the film is postannealed in the reduced atmosphere, such as in N_2, oxygen vacancies are generated at a relatively high temperature (above 200 °C) according to the following reaction:

$$O_o(\text{Oxygen ion at its normal site}) \rightarrow Vo^{2+}(\text{Oxygen vacancy}) + 2e^- + 1/2O_2.$$

The oxygen vacancies and space charges (electrons) are produced in the grain boundaries, resulting in low-frequency dielectric relaxation. Higher postannealing temperature in N_2, such as 550 °C, will produce more oxygen vacancies and space charges, thus, more obvious dielectric relaxation can be observed. On the other hand, when postannealing in an oxygen atmosphere, the above reaction will be reversed and the oxygen vacancies will be compensated, leading to the disappearance of the dielectric relaxation. Moreover, when the postannealing temperature is as high as 550 °C, not only oxygen vacancies in the grain boundaries are compensated, but also the oxygen vacancies in part of the originally oxygen-deficient grains near the boundaries. Thus, effectively, the grain boundary layer is increased, causing the dielectric constant to decrease.

In summary, CCTO thin films with high dielectric constant were successfully prepared on $Pt/Ti/SiO_2/Si$ (100) substrates by pulsed-laser deposition (PLD). Microstructure studies reveal that the films are polycrystalline with square shaped crystals on the surface. The dielectric properties and their temperature dependence for the Pt/CCTO/Pt capacitors are comparable with those obtained in the epitaxial CCTO films deposited on oxide substrates, and were found to be very sensitive to the postannealing atmosphere and temperature. Our study demonstrates that postannealing in nitrogen atmosphere produces strong low-frequency dielectric relaxation as the annealing temperature increases, while annealing in oxygen atmosphere at high temperature suppresses the relaxation and decreases the dielectric constant of the thin films. Such results can be explained using the insulating grain-boundary mechanism.

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