Journal of Alloys and Compounds 743 (2018) 570–575

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Non-Ohmic properties of $MgTiO_3$ doped $CaCu_3Ti_4O_{12}$ thin films deposited by magnetron sputtering method

Mi Xiao*, Lei Li, Ping Zhang**

School of Electrical and Information Engineering, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Received 6 November 2017
Received in revised form
2 January 2018
Accepted 14 January 2018
Available online 16 February 2018

Keywords:
CCTO
Non-Ohmic properties
Magnetron sputtering method
Double Schottky barrier model

ABSTRACT

$CaCu_3Ti_4O_{12}$-x$MgTiO_3$ (x = 0, 0.05, 0.1 and 0.2) thin films were prepared through magnetron sputtering method and sintered at 850 °C for 1 h. Second phase of CuO and TiO_2 were detected in $MgTiO_3$ doped ceramic targets and $CaTiO_3$ phase was observed when x = 0.2. SEM results showed that grain size increased with $MgTiO_3$ doping, which is corresponding to the decrease of threshold voltage. Remarkable non-Ohmic behaviors of all samples were observed at different temperatures. Nonlinear coefficient increased from 2.803 (x = 0) to 3.799 (x = 0.2) and Schottky barrier height increased firstly then decreased as $MgTiO_3$ doping. Double Schottky barrier model was used to explain the non-Ohmic characteristic of CCTO thin films.

1. Introduction

Due to the ongoing miniaturization trend of semiconductor devices, $CaCu_3Ti_4O_{12}$ (CCTO) has attracted enormous attention for its remarkable dielectric properties. It exhibits giant dielectric constant over 10^4 at room temperature (RT) and strong stability in a wide temperature range of about 100–400 K at low frequency [1–3]. So far, many theories were put forward to explain the extraordinary dielectric properties of CCTO. Both intrinsic effects [4,5] and extrinsic effects [6,7] have been investigated, and the most acceptable explanation is the Internal Barrier Layer Capacitor (IBLC) [8] model, which suggests that CCTO is electrically heterogeneous and consists of insulating grain boundaries and semiconducting grains. In 2004, excellent non-Ohmic behavior of CCTO was observed by Chung et al. [9] by using microcontact I-V measurements and Kelvin probe force microscopy. It was found that the nonlinear coefficient of CCTO is much greater than that of traditional ZnO varistors. Since then, much work has been done to investigate the internal mechanism of non-Ohmic behavior of CCTO. Jutapol et al. [10] investigate the influence of grain boundary density on non-Ohmic characteristic by comparing the microstructure of different samples. Ekaphan et al. [11] attributed this behavior to the existence of Schottky barrier between semiconducting grains and insulating grain boundaries. Xiao et al. [12] proposed a metal-insulator-semiconductor (MIS) structure to explain this behavior, in which second phase CuO acted as an insulating layer between top electrode and CCTO thin film. At present, the Double Schottky Barriers (DSB) model [13] located at insulating grain boundaries between symmetrical semiconducting grains was most widely used to explain the non-Ohmic behaviors of CCTO.

Element substitution is a substantial way to investigate the origin of the non-Ohmic behaviors as well as modify the non-Ohmic properties of CCTO material. Xu et al. [14] prepared $CaCu_{3-x}Zn_xTi_4O_{12}$ ceramics in which the largest nonlinear coefficient 6.4 and the lowest breakdown voltage 76 V/mm were obtained when x = 0.06. Jakkree et al. [15] investigated the influence of co-doping of Y ions in Ca sites and Mg ions in Cu sites and the non-Ohmic properties of CCTO ceramics were increased significantly. And the substitution of Sn in Ti sites [16] and Sr in Ca sites [17] were also investigated. The non-Ohmic behaviors are also found to be associated with the microstructure of CCTO material [9,18]. The grain size has a direct influence on the volume fraction of grain boundaries and the number of barriers existed between grains and grain boundaries which will finally have an impact on the non-Ohmic behaviors. The grain boundary performance of CCTO can be tuned by introducing a second phase and making a ceramic composite system [19–21] which have a direct influence on the breakdown voltage and nonlinear coefficient of CCTO

* Corresponding author.
** Corresponding author.
E-mail addresses: xiaomitju@yeah.net (M. Xiao), zptai@163.com (P. Zhang).

https://doi.org/10.1016/j.jallcom.2018.01.202

material.

It is important to develop films with good performance to meet the miniaturization trend of electronic devices. While the non-Ohmic properties of CCTO thin films are much weaker than that of bulk material. The high dielectric loss and low nonlinear coefficient may limit the further application of pure CCTO thin films. Yuan et al. [22] have investigated the effect of $MgTiO_3$ on the dielectric and varistor properties of CCTO ceramics, in which the nonlinear coefficient and breakdown voltage can be tuned by controlling the ratio of CCTO and $MgTiO_3$ composites. To optimize the performance of CCTO thin films material, introducing a second phase of $MgTiO_3$ with low dielectric loss and high breakdown voltage may be a good choice.

In this work, $CaCu_3Ti_4O_{12}$-x$MgTiO_3$ (x = 0, 0.05, 0.1 and 0.2) thin films with obvious non-Ohmic behaviors were prepared through magnetron sputtering method. The effects of $MgTiO_3$ doping on the microstructure and non-Ohmic behaviors of CCTO thin films were investigated, and the possible mechanism was explained through DSB model.

2. Experimental procedure

To investigate the effects of $MgTiO_3$ doping on the non-Ohmic behavior of CCTO thin film, $MgTiO_3$ was prepared in advance by using traditional solid-state method with $(MgCO_3)_4\cdot Mg(OH)_2\cdot 5H_2O$ and TiO_2 as starting materials, they were weighted, ball milled for 12 h and the slurries were dried and calcined at 1100 °C for 1 h. Then stoichiometry amount of $CaCO_3$, TiO_2, CuO and $MgTiO_3$ were weighted according to the formula of $CaCu_3Ti_4O_{12}$-x$MgTiO_3$, where x = 0, 0.05, 0.1 and 0.2 respectively. The mixtures were ball milled for 6 h. The obtained slurries were dried and calcined at 950 °C for 2 h and ball milled again for another 6 h. Then the dried powders were mixed with 8 wt% paraffin and pressed into disks with 73–75 mm in diameter and 5 mm in thickness with pressure of 30 MPa for 30 min. CCTO-$MgTiO_3$ targets were obtained after sintered at 1080 °C for 2 h, and the resulted targets were about 60 mm in diameter. Small pellets were also prepared with 15 mm in diameter and 1 mm in thickness, which were used for XRD and SEM after sintered at the same condition.

$CaCu_3Ti_4O_{12}$-x$MgTiO_3$ (x = 0, 0.05, 0.1 and 0.2) thin films were prepared using magnetron sputtering method. Pt/Ti/SiO_2/Si substrates were ultrasonically cleaned with acetone, anhydrous ethanol and deionized water respectively for 5min. The target was pre-sputtered for 1min to eliminate contaminations. The actual sputtering process was conducted under a constant sputtering power 120w for 2 h with a fixed distance between target and substrate. Pressure in the vacuum chamber was controlled to be 0.8 pa with argon flow rates of ~40 sccm. The obtained thin films were sintered at 850 °C for 1 h.

The crystal structures of all the samples were investigated by X-ray diffraction (XRD, Rigaku, D/Max, 2500 V/PC) at RT over 2θ range of 20°–80°. The surface and cross section morphology and microstructure were examined by field emission scanning electron microscope (SEM, ZEISS MERLIN Compact, Germany). The non-Ohmic behavior of the thin films were measured by semiconductor parameter analyzer (Keilthley 4200-SCS).

3. Results and discussion

3.1. XRD analysis

X-ray diffraction patterns of the pure CCTO and $MgTiO_3$ doped ceramics are displayed in Fig. 1. All diffraction peaks of the CCTO were detected and matched well with the standard diffraction patterns (ICSD 89-59522) in all the samples. There wasn't any noticeable second phase in pure CCTO sample, which indicated that single pure CCTO phase was formed. Second phase of CuO and TiO_2 were detected in $MgTiO_3$ doped samples, and $CaTiO_3$ phase was detected when x = 0.2, which means Cu^{2+} and Ca^{2+} in CCTO lattice might be displaced during the sintering process. As doping contents increased, diffraction peaks shifted towards higher angle which is shown in the inset of Fig. 1, indicating the decrease of interplanar spacing. The reason can be attributed to the substitution of Mg^{2+} ions with smaller ionic radius (0.72 Å) for Cu^{2+} (0.73 Å) and Ca^{2+} (0.99 Å).

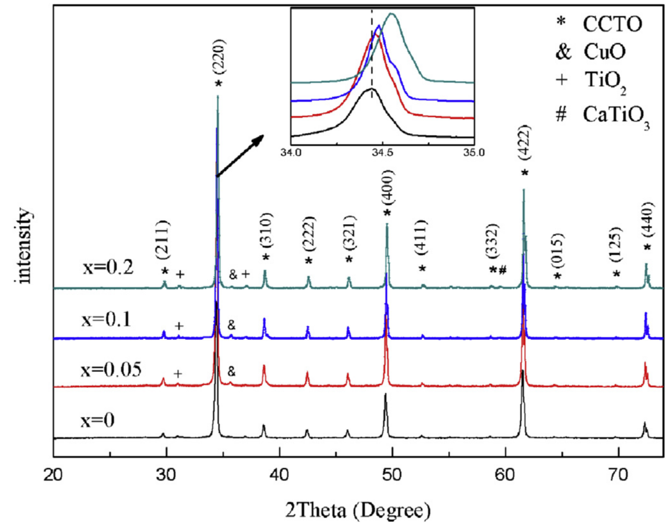

Fig. 1. XRD patterns of $CaCu_3Ti_4O_{12}$-x$MgTiO_3$ ceramic targets.

Fig. 2 shows the XRD patterns of the $CaCu_3Ti_4O_{12}$-x$MgTiO_3$ (x = 0, 0.05, 0.1 and 0.2) thin films through magnetron sputtering method, in which the main diffraction peaks of (220), (400) and (440) of CCTO can be detected in all samples. A slight shifting of diffraction peak towards higher angle as $MgTiO_3$ doped can also be seen and shown in the inset of Fig. 2. No second phase were detected in all the thin films. An intriguing phenomenon can also be found that with the doping of $MgTiO_3$, the height of (400) diffraction peak decreased firstly and then increased, while the height of (220) and (440) diffraction peaks decreased monotonously. The

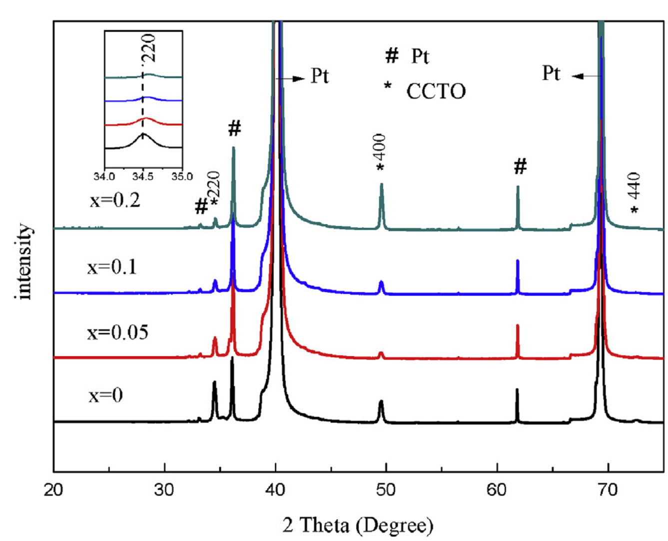

Fig. 2. XRD patterns of $CaCu_3Ti_4O_{12}$-x$MgTiO_3$ thin films sintered at 850 °C.