Materials Science in Semiconductor Processing 16 (2013) 1297–1302

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Photo-assisted metal-organic chemical vapor deposition of $CaCu_3Ti_4O_{12}$ (CCTO) thin films

N. Gupta [a,*], C. McMillen [b]

[a] Holcombe Department of Electrical and Computer Engineering, Riggs Hall, Clemson University, Clemson, SC 29634, USA
[b] Department of Chemistry, Clemson University, Clemson, SC 29634, USA

ARTICLE INFO

Available online 24 April 2013

Keywords:
Photo-assisted MOCVD
Calcium copper titanate
Thin film
Dielectric

ABSTRACT

Calcium copper titanate ($CaCu_3Ti_4O_{12}$) or CCTO is one of the most researched giant dielectric constant materials in recent years. In the present work, incoherent light source based photo-assisted metal-organic chemical vapor deposition (MOCVD) has been used to prepare CCTO thin films on Si/SiO_2 substrates. Key to this unique processing technique is the use of UV radiation as an additional source of energy in conjunction to the thermal energy. The given Photo-assisted MOCVD processing resulted in polycrystalline CCTO growth on a SiO_2 surface. Powder X-ray diffraction and scanning electron microscopy were performed to analyze structural and compositional properties of the CCTO thin film. Ellipsometric measurements indicated a refractive index of 3.03 for the CCTO thin film.

1. Introduction

Since the invention of the first capacitor in the 1700s, researchers have suggested several high dielectric constant materials including $BaSrTiO_3$, $PbLaZrTiO_3$, etc., to create energy storage capacitors with high energy density. In recent years, one of the most researched materials with giant dielectric constant is calcium copper titanate ($CaCu_3Ti_4O_{12}$) or CCTO which is a perovskite-like structured ceramic. The high dielectric constant of CCTO (10,286 at 100 kHz) was first reported by Subramanian et al. in 2000 [1]. Subsequently, several methods were explored to synthesize this material in bulk as well as in thin films on various substrates. These methods include solid state synthesis [1], chemical method [2], sol–gel [3], pulse LASER deposition (PLD) [4], and metalorganic chemical vapor deposition (MOCVD) [5]. Recently, Khaleeq-ur-Rahman et al. used PLD technique to deposit thin films of strontium hexa ferrite ($SrFe_{12}O_{19}$) [6].

The origin of the very high dielectric constant in CCTO is still a topic of disagreement among researchers. The possible mechanisms for the very high dielectric constant in CCTO are partly explained by the internal barrier layer capacitance (IBLC) model, consisting of grain boundary effects and the Maxwell–Wagner effect, focusing on sub-grain boundaries [7]. However, IBLC does not completely explain this effect in a single crystal material. In 2005, Wu et al. reported another model similar to IBLC for single crystal CCTO [8]. Recently, several researchers have also asserted that physical, structural, and stoichiometric properties of the dielectric film, including defects cause different dielectric properties [9,10]. Thus, the origin of the very high dielectric constant in CCTO is still not apparent. However, the value of the dielectric constant of un-doped CCTO is variously reported from 2×10^2 to 8×10^4 [11,12]. This variation of the dielectric constant implies a strong dependence of dielectric properties of CCTO on the fabrication process.

In several areas of semiconductor manufacturing, rapid photothermal processing (RPP) has proven itself a superior technique for depositing dielectric thin films with very low leakage current, low defect density and good reliability at low thermal budget [13–16]. For the very first time, Singh

* Corresponding author. Tel.: +1 864 633 6426; fax: +1 864 656 5917.
E-mail addresses: ngupta@g.clemson.edu (N. Gupta), cmcmill@clemson.edu (C. McMillen).

1369-8001/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2013.03.013

et al. exploited the advantages of photo-assisted CVD in their work published in 1991[17]. This unique processing technique uses photoenergy as an additional source of energy with thermal energy. From the electromagnetic spectrum, only the photons with wavelength more than about 800 nm contribute to thermal effects, while photons between 400 nm and 800 nm contribute to both thermal and quantum effects [18]. Photons with wavelength less than 400 nm provide quantum effects without any undesirable effect. The quantum effects have the following implications for the photo-assisted CVD process [19]:

1. The bulk and surface diffusion coefficients are increased for a given processing temperature.
2. The processing cycle time is reduced.
3. Due to lower microscopic defects, higher performance, better reliability and yield are achieved.

The Xenon flash lamp used in this work emits photons with wavelength from 200 nm to more than 1000 nm, as shown in Fig. 1 [20]. The spectrum emitted from the Xenon flash lamp provides both thermal and quantum effects and produces high quality thin film of the material being deposited.

2. Experimental details

2.1. Photo-assisted MOCVD system

A custom-designed non-commercial MOCVD system with an incoherent light source, as illustrated in Fig. 2, was used to deposit high quality CCTO thin films on Si/SiO_2 substrates. The substrates were prepared by growing silicon dioxide on p-type (1 0 0) silicon wafers in a furnace using wet oxidation at 1050 °C for 4 h, to achieve an oxide thickness of about 500 nm. For the photo-assisted MOCVD process, the calcium and copper precursors ($Ca(TMHD)_2$ and $Cu(TMHD)_{2)}$ were purchased from Strem chemicals while the Titanium precursor, Titanium(IV) isopropoxide ($C_{12}H_{28}O_4Ti$), was purchased from Alfa Aesar. In the past, we have used 2,2,6,6-tetramethyl-3,5-heptanedionato (TMHD) complexes to create several high quality films [21,22]. All the precursors used in this work were used as purchased without any modifications. Except for the nitrous oxide (N_2O), all gases used in the process were ultra-high purity (UHP). Based on our previous experience of depositing dielectric films using CVD, nitrous oxide and UHP oxygen were used as the reaction gases [22]. UHP nitrogen was used as the carrier gas to transport precursor vapors from the precursor chamber to the deposition chamber. MKS mass flow controllers (MFC) were used to control gas flow rates for all the gases. All the precursors were kept in heated stainless steel chambers and connected by a heated delivery line to the deposition chamber as shown in Fig. 2. The temperature of delivery line was maintained at 180 °C for all the experiments. The temperatures in the precursor chambers and delivery lines were monitored with type K thermocouples and controlled with LabView modules. The UV source, MFCs and solenoid gas valves were also controlled with LabView Modules to improve process effectiveness. Table 1 shows a summary of optimized process parameters, as used for sample no. P97, including precursor temperatures and flow rates for different gases used in the process. The base pressure and deposition pressure for the process was 2×10^{-2} Torr and 1.2 Torr, respectively.

2.2. Process flow of photo-assisted MOCVD

A thermally oxidized p-type (1 0 0) Si wafer was loaded into the MOCVD deposition chamber. The substrate was cleaned in-situ in forming gas (20% UHP H_2 and 80% UHP N_2) at 925 °C for 5 min. Ca and Cu precursors were heated in vacuum at 230 °C and 120 °C respectively, while the Ti precursor was used at room temperature. After cleaning the substrate in-situ, the substrate was heated to the deposition temperature of 750 °C and the deposition process was carried out for 15 min. After deposition, the

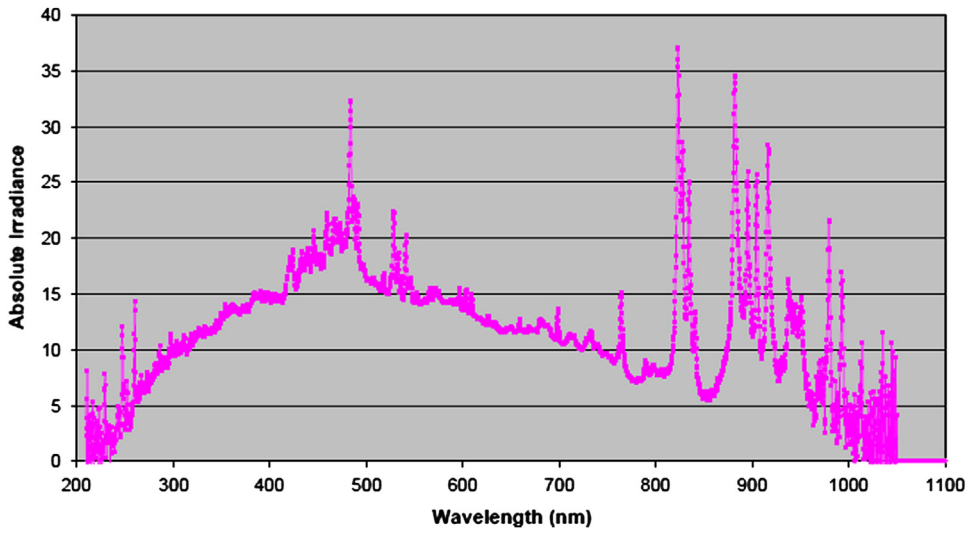

Fig. 1. Spectrum of xenon flash lamp used in photo-assisted MOCVD system.