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Fabrication and characterization of $CaCuO_2/CaCu_2O_3$ thin films with enhanced third-order nonlinear properties

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In this work, poly-crystalline $CaCuO_2/CaCu_2O_3$ thin films were deposited on quartz substrates using radio frequency (RF) magnetron sputtering and subsequent annealing. The deposition process was performed at room temperature under an oxygen partial pressure of 4×10^{-2} Pa at a speed of 2 Å/s. The crystalline structure, distribution of the particles and size of the elements of the as-prepared and $CaCuO_2/CaCu_2O_3$ thin films were individually acquired and discussed in detail. Subsequent annealing was found to modify the composition, structure and morphological characteristics of the as-prepared thin film, resulting in changes of the film quality and, thereby, improving the nonlinear optical (NLO) response of the film. The sign and magnitude of third-order nonlinear susceptibility $\chi^{(3)}$ of the as-prepared and $CaCuO_2/CaCu_2O_3$ thin films were determined using the top-hat Z-scan technique performed at 532 nm with a laser duration of 190 fs. The results show that annealed $CaCuO_2/CaCu_2O_3$ thin film exhibits a fast NLO response with a third-order nonlinear susceptibility $\chi^{(3)}$ of 1.1×10^{-12} esu, which is higher than that of the as-prepared thin film. The results indicate that $CaCuO_2/CaCu_2O_3$ thin films have potential applications in nonlinear optics.

1. Introduction

Over the past few years, studies on cuprate superconductors have attracted increasing attention [1–3], as they may have a significant effect on our understanding of the structure and the mechanism of the high temperature superconductors, such as the unwonted pairing symmetry phenomenon [4] and quantum phase transition [5]. Thus, cuprates could be vital precursors in the preparation of Cu-O chain superconductors. Certainly, cuprates with special Cu-O chain structures are not only useful in superconductivity but also meaningful in optical applications including fast response and large optical nonlinearility. As for applications in nonlinear photonics, ferroelectric films like $BaTiO_3$ [6], $CaTiO_3$ [7] and Ca_2CuO_3 [8] films have been systematically studied, spawning a wave of investigations on film materials with good optical nonlinearility. In previous reports [9–11], scholars have gravitated towards $CaCuO_2$ thin films or $CaCu_2O_3$ single crystals, mainly for the good stability of $CaCuO_2$ thin film under high pressure and the special spin-ladder structure of $CaCu_2O_3$, which cause their wide utilization in superconductivity. For instance, M Salvato [12] fabricated $CaCuO_2$ thin films on $SrTiO_3$ (001) and $NdGaO_3$ (001) by pulsed laser deposition (PLD) and discussed the transport properties and superconducting anisotropy of the single interfaces of $CaCuO_2$ and $SrTiO_3$. Additionally, single crystal $CaCu_2O_3$ was prepared by traveling solvent floating zone (TFSZ) method by K. G. Lisunov [13], and its nearest-neighbor (Cu-O) hopping conductivity mechanism was also elaborately investigated and explained. In other words, these studies [14] have focused much of their attention on cuprates related to superconductivity. However, composites of cuprates, as a result of their unique configurations, exhibit better properties than some of their constituents. One typical example of this is third-order NLO property, especially for film materials.

The fast progress of nonlinear optics has resulted in a growing number of people searching for more suitable nonlinear materials, which could be practically applied in optical switches and limiters. Large third-order optical non-linearity was a basic prerequisite for nonlinear materials in practical applications. The composite materials of $CaCuO_2$ and $CaCu_2O_3$, which are two typical cuprates compounds, possess several attractive properties, including high

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dielectric constant [15], large spontaneous polarization [16], and good optical non-linearity [17] for their charge transfer and photons interactions [18–20] between the adjacent atoms. Furthermore, film materials, due to their high transparency, low roughness and easy fabrication, have been widely used in various electron-optical devices in recent decades. Therefore, more studies [21] have been performed to prepare NLO films, such as CuO, Ca_2CuO_3, and some other cuprates. Frankly speaking, these studies managed to identify the films with better optical nonlinearility, which allow us to make progress in these fields.

Thus, a traditional RF magnetron sputtering method [22] with air annealing process was adopted to prepare a $CaCuO_2/CaCu_2O_3$ thin film in this paper. The third-order nonlinearility of the $CaCuO_2/CaCu_2O_3$ thin film was measured by Z-scan technique, and compared with the as-prepared thin film. The results reveal that the mixed cuprate thin film of $CaCuO_2/CaCu_2O_3$ own a better nonlinear response than the as-prepared film, indicating its potential applications in nonlinear optics and related area.

2. Experimental details

2.1. Materials

Calcium carbonate and copper oxide were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Quartz glass sheets, as substrates, were purchased from Hefei Crystal Materials Technology Co. Ltd. (Hefei, China). All of the reactants were analytical grade and were directly used as received without any further purification.

2.2. Fabrication of $CaCuO_2/CaCu_2O_3$ thin films

$CaCuO_2/CaCu_2O_3$ thin films were fabricated on quartz glass substrates using RF magnetron sputtering from a Ca_2CuO_3 target in an Ar and O_2 (4:1) atmosphere [23] followed by annealing. The Ca_2CuO_3 target [24] was prepared by the solid-state method [25] in air. The $CaCO_3$ and CuO powders were ground in an agate mortar, then thoroughly mixed at a theoretical stoichiometric ratio and calcined at 950 °C for 24 h. The obtained powder was pressed into a plate and fired at 900 °C for 15 h. Finally, a Ca_2CuO_3 target with a diameter of 50 mm was acquired, as shown in Fig. 1a on the left. Binding the Ca_2CuO_3 target and Cu target tightly together with melting indium is important before usage. The sputtering system is equipped with a load lock chamber for fast and convenient substrates exchange. The quartz glass substrates were cleaned in ethanol and acetone several times prior to their introduction in the deposition chamber. The sputtering chamber was pumped down to 5×10^{-4} Pa before O_2 and Ar were introduced into the chamber. In this investigation, the distance between the Ca_2CuO_3 target and substrates was fixed at 120 mm. It is mentioned that heating was not performed on the substrates. The more detailed sputtering conditions are listed in Table 1. Finally, air annealing was performed in a muffle furnace at 750 °C for 1 h. The heating rate from room temperature to the annealing temperature was fixed at 150 °C h^{-1}.

3. Characterization

The crystal structure of the two films was identified by X-ray diffraction (XRD) with an X-ray diffract meter (D8 Focus, Bruker, Germany) over the 2θ range of 10–80° using Cu Ka radiation. As regarding to Uv–vis absorption and transmittance, a UV-2600 spectrometer was used to acquire the spectra in the range of 200–1100 nm. To obtain the surface morphology, particle distribution and chemical composition of the films, field-emission scanning electron microscope (FESEM) measurements were performed using a JEOL-JSM-6700F scanning electron microscope equipped with an X-ray energy dispersive spectroscope (EDS). STEM and high-resolution TEM (HRTEM) measurements were carried out with a FEI Tecnai F20 at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted to determine the elemental composition using an Axi Ultra DLD spectrometer with monochrome Al-Ka as the excitation source. The NLO measurements were performed using a single-beam Z-scan technique. A picosecond laser system, which consisted of a mode-locked Ti: Sapphire oscillator (Tsunami, Spectra-Physics) and a regenerative amplifier (Spitfire), was used as a light source. The output average power of the system is about 200 mW with a repetition rate of 20 Hz, a pulse duration of 190 fs and a wavelength at 532 nm. The laser beam with 0.1 μJ pulse energy was focused on the film by a lens of 10 cm focal length. The transmitted light after the sample was split into two beams, one for open-aperture and the other for closed aperture operations. The beams were collected by two photodiode detectors connected with a Boxcar integrator. All measurements were carried out at room temperature.

4. Results and discussion

4.1. XRD analysis

Both the prepared Ca_2CuO_3 target and its XRD pattern are shown in Fig. 1a and b respectively. Obviously, the main peaks agree well with JCPDS No.34-0284 Ca_2CuO_3, and several extra peaks are

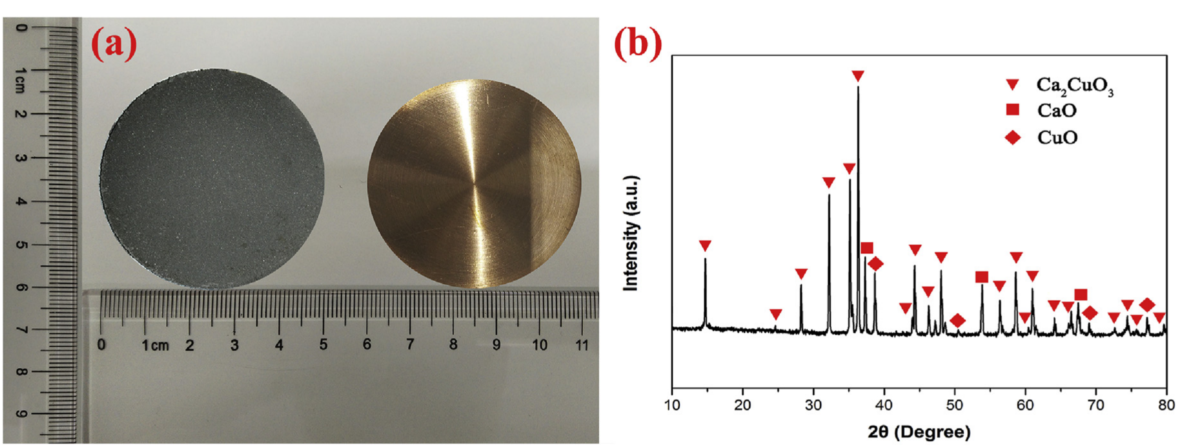

Fig. 1. (a) The synthesized Ca_2CuO_3 target and (b) its XRD pattern.