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Fabrication and electrical properties of $YBa_2Cu_3O_{7-x}$ thin film prepared by Sol-gel method for uncooled infrared detectors

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In this study, we fabricated the semiconducting YBCO thin film by sol-gel method. Precursor solution had been fabricated using Y acetate, Ba hydroxide and Cu acetate as starting materials, and propionic acid (PPA) and propylamine (PA) as solvent. The YBCO precursor solution was passed through a syringe filter and spin-coated on the SiO_2-coated Si substrate using a spinner operated at 3,000 rpm for 20 sec. YBCO thin films were dried at 500 °C for 2 h and annealed at 750 °C for 1 h. Then, the structural and electrical characteristics of YBCO thin films were measured with a variation of solvent ratios. The films PPA/PA at 8 : 1 showed the more obvious $YBa_2Cu_3O_{7-x}$ phase and tetragonal phase. The thickness of all the films was approximately 250 ~ 330 nm and the average grain size of the YBCO thin films PPA/PA at 8 : 1 was about 60 nm. Temperature resistance coefficient (TCR), responsivity and detectivity of the YBCO thin films PPA/PA at 8 : 1 were -3.3%/K at room temperature, 15.94 V/W and 2.44×10^6 cmHz1/2/W, respectively.

Key words: YBCO, Thin film, Sol-gel.

Introduction

There is a great interest in infrared (IR) detection for a wide range of applications from military to civilian night vision, such as detection of flames for fire alarms, heat emitted by warm objects for intruder detection, and thermal imaging applications in transportation and medicine. Commonly used materials for infrared detectors (pyroelectric detector type) are triglycene sulphate(TGS), lithium tantalite($LiTaO_3$), $(Ba,Sr)TiO_3$, $Pb(Zr,Ti)O_3$, et al [1-3]. However, little has been studied on uncooled infrared detectors using the non-superconductor phase of $YBa_2Cu_3O_{7-x}$(YBCO) thin films. These infrared detectors will utilize the oxygen deficient phase of $YBa_2Cu_3O_{7-x}$ and will be operated at near room temperature. Generally, bolometers will be made of the semiconducting $YBa_2Cu_3O_{7-x}$ on SiO_2 or Si_3N_4 and exhibit a high rate of resistance change with the variation of temperature, dR/dT. This material shows better pyroelectric properties than other uncooled materials and is comparable to cooled HgCdTe.

Obviously, the superconducting bolometer exhibits a temperature coefficient of resistance much larger than the TCR of any semiconducting material operating at room temperature. If we choose to cool the device, which implies the extra burden of a cooling system, the bolometric sensing material will offer—together with lower noise level—a better thermal sensitivity. Nevertheless, uncooled bolometers have become the dominating technology for the majority of civil and military imaging applications in the infrared (IR) range [4]: thermography, medical imaging, fire fighting, predictive maintenance, industrial process control, night vision. YBCO is best known as a high temperature superconductor. The optical and electronic properties of $YBa_2Cu_3O_{7-x}$ are determined by its oxygen stoichiometry. For x = 1, YBCO possesses an orthorhombic crystal structure, exhibits metallic conductivity, and becomes superconductive upon cooling below its critical temperature. As x is increased to 0.5, the crystal undergoes a phase transition to a tetragonal structure and it exhibits semiconducting conductivity characteristics as it exists in a Fermi glass state. As x is increased further above 0.5, YBCO becomes a Hubbard insulator with a well defined energy gap on the order of 1.5 eV [5]. Semiconducting thin film, YBCO possesses a high pyroelectric coefficient at room temperature, two hundred times greater than other thin film materials. This enables high detectivity pyroelectric thermal detectors to be fabricated on micromachined thermal isolation structures integrated on CMOS read-out circuitry, since the amorphous semiconducting phase of YBCO, used in these imaging devices, is deposited at ambient temperature with no need of high temperature post-annealing. In regards to $YBa_2Cu_3O_{7-x}$ semiconductors, great progress has been made in the scientific and technological field concerning the thin film growth of perovskite-type oxides. With careful control of the processing parameters, high-quality YBCO thin films with high critical current densities and high transition temperatures have been prepared by techniques such as

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evaporation, sputtering, chemical vapor deposition, and laser ablation. [6-8] In this study, semiconducting YBCO thin films were prepared using the sol-gel method, which were spin-coated in the SiO_2-coated Si substrate using YBCO alkoxide solutions. We also investigated the structural and electrical properties of YBCO thin films with variation of solvent ratios for application in IR detectors.

Experimental Procedure

Using the sol-gel method, YBCO precursor solutions were prepared from the starting materials yttrium acetate tetrahydrate [$Y(CH_3COO)_3 4H_2O$], copper acetate monohydrate [$Cu(CH_3COO)_2 H_2O$], barium hydroxide [$Ba(OH)_2 8H_2O$], and the solvent propionic acid (PPA) and propylamine (PA). The stoichiometric molar ratio of yttrium acetate, barium hydroxide and copper acetate is 1 : 2 : 3. The oxide concentration of the solution is 0.1 ~ 0.6 mol/l, as control of the ratio between the propionic acid and propylamine adjusts the viscosity to 10 ~ 200 cp. Therefore, the solution was fabricated by the ratio of solvent to adjust the viscosity. In addition, diethanolamine was used to increase the wetting and to reduce the surface tension of the solution above the polished substrate.

The YBCO precursor solution was passed through a syringe filter and spin-coated on the SiO_2 (200 nm)/p-Si(100) substrates using a spinner operator at 3,000 rpm for 20 sec to form the first layer. These YBCO thin films were air-dried at 200 ~ 250 °C for several minutes. Generally, one coating gives a thickness of 60 ~ 80 nm. This coating/drying procedure was repeated several times to get a desired thickness. The multicoated thin films were dried at 450 ~ 550 °C for 1 ~ 3 h to remove the organic materials, and annealed at 650 ~ 800 °C for 1 h in Ar/O_2 atmosphere to crystallize them into a tetragonal structure. The crystalline structures of the YBCO thin films were analyzed by X-ray diffraction (XRD) with CuKemission. The surface and cross-sectional microstructures of films were examined using field-emission scanning electron microscopy (FE-SEM). The electrodes were fabricated by screen printing the Ag paste. The electrical properties of the specimens were measured using a LCR meter (Fluke 6306, USA) and an electrometer (Keithley 6517A, USA) for IR detector applications.

Results and Discussion

Fig. 1 shows the X-ray diffraction pattern of YBCO thin film printed on SiO_2/Si substrate for variation of solvent ratio. All YBCO films showed $YBa_2Cu_3O_{7-x}$ phase and tetragonal structure. YBCO films PPA/PA at 2 : 1 and 4 : 1 showed the second phase, such as BaO, CuO and $BaCu_3O_6$. YBCO thin films PPA/PA at 8 : 1 showed the more obvious $YBa_2Cu_3O_{7-x}$ phase, a little second phase was observed. However, the PPA/PA at 10 : 1 showed 8 : 1 compared to the less obvious $YBa_2Cu_3O_{7-x}$ phase due to the excess propionic acid ratio.

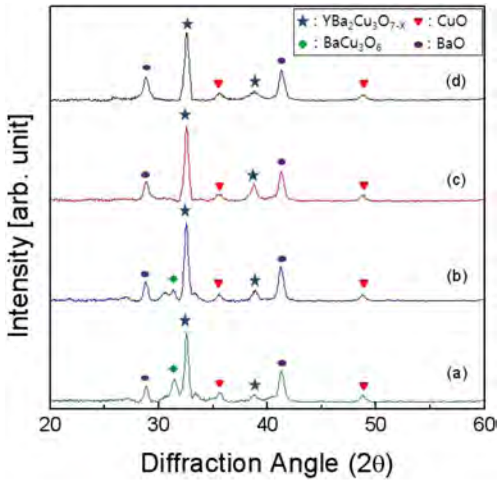

Fig. 1. XRD patterns of YBCO thin films as a function of solvent ratio; (a) 2 : 1, (b) 4 : 1, (c) 8 : 1, (d) 10 : 1.

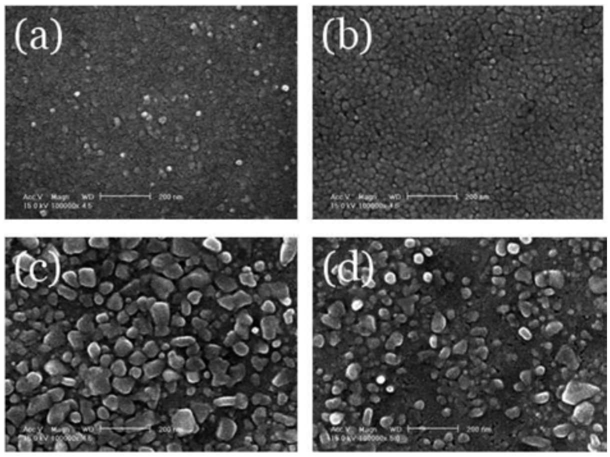

Fig. 2. Surface SEM micrographs of YBCO thin films as a function of solvent ratio; (a) 2 : 1, (b) 4 : 1, (c) 8 : 1, (d) 10 : 1.

Fig. 2 shows the surface SEM micrographs of YBCO thin films with variation of solvent ratio. The grain size increased with increasing annealing temperature, the YBCO thin films solvent ratio at 8 : 1 showed the average grain size of about 60 nm. The YBCO thin films PPA/PA at 2 : 1 and 4 : 1 showed the small grain with large grain boundaries layers due to the high viscosity of the solution. Also, the film PPA/PA at 10 : 1 showed the pores due to the excess propionic acid ratio.

Fig. 3 shows the cross-sectional SEM micrographs of YBCO thin films with variation of solvent ratio. The thickness of all the films was approximately 250 ~ 330 nm, and the film thickness dependence on the solvent ratio was observed. Viscosity of the solution is changed by the solvent ratio and film thickness depending on this viscosity. All films showed the relatively flat surface morphology and the pores distributed inside the films.

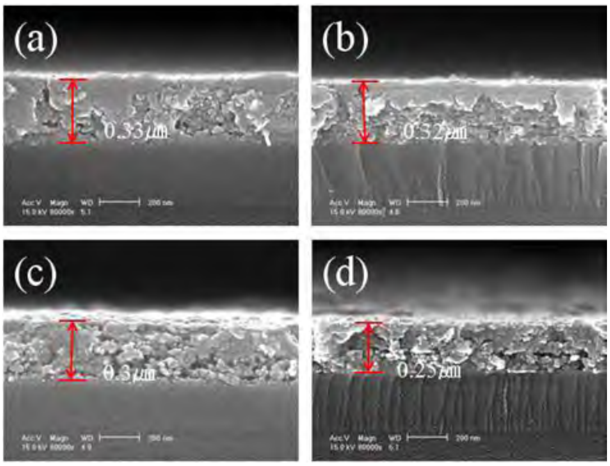

Fig. 3. Cross-sectional SEM micrographs of YBCO thin films as a function of solvent ratio; (a) 2 : 1, (b) 4 : 1, (c) 8 : 1, (d) 10 : 1.

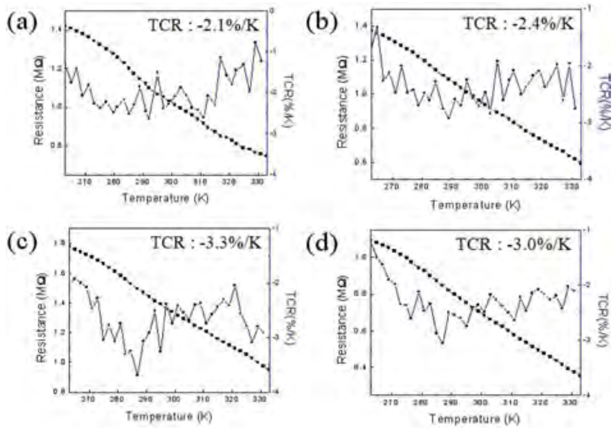

Fig. 4. Electrical resistance and TCR properties of YBCO thin films as a function of solvent ratio; (a) 2 : 1, (b) 4 : 1, (c) 8 : 1, (d) 10 : 1.

Fig. 4 shows the temperature coefficient of resistance (TCR) of YBCO thin films with the variation of solvent ratio. All YBCO thin films showed the NTCR (negative temperature coefficient of resistance) properties, which means that the electrical resistance decreased with increasing the temperature, of typical semiconductor materials. YBCO thin films PPA/PA at 8 : 1 showed the highest values of 59.7 MΩ and -3.3%/K at room temperature, respectively. This is because the grain size of single crystalline increased with decreasing the second phase, as shown in Fig. 2. However, in the YBCO thin films PPA/PA at 10 : 1, electrical resistance and TCR decreased with decreasing the grain size and the pores.

Fig. 5 shows I-V characteristics of YBCO thin films with the variation of solvent ratio, with the current-voltage characteristics of the bolometer showing a linear graph. Likewise, current-voltage characteristics of YBCO thin films show a linear graph. All YBCO thin films showed the ohmic conduction properties, however, the slope of I-V curves was changed as the applied voltage changed. This property may be understood in terms of

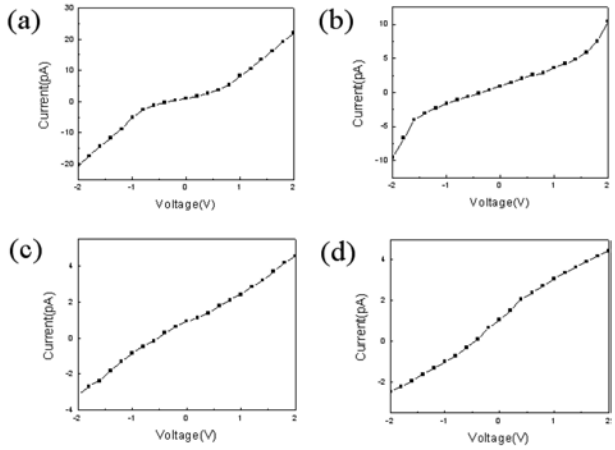

Fig. 5. I-V characteristics of YBCO thin films as a function of solvent ratio; (a) 2 : 1, (b) 4 : 1, (c) 8 : 1, (d) 10 : 1.

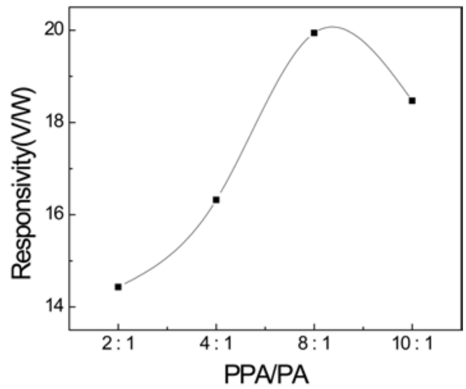

Fig. 6. Responsivity of YBCO thin films with variation of solvent ratio.

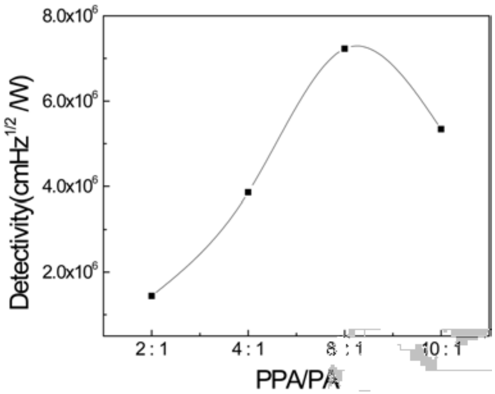

Fig. 7. Detectivity of YBCO thin films with variation of solvent ratio.

the effect of the difference of work function between the semiconducting YBCO thin films and Ag electrode.

Considering the alignment between the incident light and the device, a blackdody furnace temperature of 600 K was used to measure the bolometer application of YBCO thin films. Figs. 6 and 7 show the voltage responsivity and detectivity of YBCO thin films with the variation of annealing temperature. Voltage responsivity (Rv), that is, the ratio of the output voltage by the pyroelectric effect

Table. 1. Measuring parameters.

BBS Temperature	500 °C
Chopper Frequency	15 Hz
BBS Aperture	0.6”
Bias Voltage	1 V
Gain	25
Filter	9.46 m/9.00 ~ 10.0 m
Distance	3 cm

to the incident radiant power, was calculated using equation (1).

$$R = \frac{V_S}{EA_D}\ [\mathrm{V/W}] \qquad (1)$$

where VS is signal output, VN is Noise output, AD is detector area, E is Irradiance, f is the effective bandwidth of radiation. Detectivity (D*) is the signal-to-noise ratio of the detector when an incident infrared beam is radiated per unit area, was calculated using equation (2).

$$D^* = \frac{\sqrt{\Delta f A_D}}{NEP}\ [\mathrm{cm\ Hz^{1/2}W^{-1}}] \qquad NEP = EA_D\left(\frac{V_N}{V_S}\right) \qquad (2)$$

Table 1 shows measuring parameters of responsivity and detectivity.

The YBCO thin films PPA/PA at 8 : 1 showed maximum values of 15.94 [V/W] and 2.44×10^6 [cmHz1/2W], respectively. The maximum voltage responsivity and detectivity resulted from the high TCR and electrical resistance, as shown in Eq. (1). Also, semiconducting YBCO single phase showed the excellent electrical properties, as shown in Fig. 4.

Conclusions

In this study, we fabricated the semiconducting YBCO thin film by spin coating method. The YBCO thin films were studied property according to the variation of solvent ratio. Viscosity of the solution is changed by the solvent ratio, and film thickness depends on this viscosity. All YBCO thin films showed $YBa_2Cu_3O_{7-x}$ phase and tetragonal structure. The YBCO thin films PPA/PA at 8 : 1 showed the more obvious $YBa_2Cu_3O_{7-x}$ phase, while a little second phase was observed. All YBCO thin films showed ohmic conduction property. Temperature resistance coefficient, responsivity and detectivity of the YBCO thin films PPA/PA at 8 : 1 were -3.3%/K at room temperature, 15.94 V/W and 2.44×10^6 cmHz1/2/W, respectively.

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