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Electrical properties of semiconducting $YBa_2Cu_3O_{7-x}$ thin film with variation of oxygen partial pressure

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$YBa_2Cu_3O_{7-x}$ (YBCO) is the material of choice for second-generation superconducting wires and is the only current option for critical current density (J_c)> 1 MA/cm^2 at 77 K [1]. YBCO belongs to a class of copper oxides well known for their superconducting properties. Its conduction properties can be changed from metallic ($0.5 < x < 1$) to insulating (0x0.5) by suitably decreasing the oxygen content [2]. The structural, electrical and optical properties of $YBa_2Cu_3O_{7-x}$ can be varied by adjusting the oxygen content x [3, 4]. As x is decreased 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. YBCO precursor solutions were prepared by the sol-gel method YBCO films were fabricated by the spin coating method, and structural and its electrical were studied at various oxygen partial pressures. The films Ar/O_2 at 7 : 3 showed the more obvious $YBa_2Cu_3O_{7-x}$ phase and tetragonal phase. The thickness of all the films was approximately 0.23 ~ 0.31 µm and the average grain size of the YBCO film Ar/O_2 at 7 : 3 was about 50 nm. Temperature resistance coefficient (TCR), responsivity, and detectivity of the YBCO film Ar/O_2 at 7 : 3 were 3.2%/K at room temperature, 14.72 V/W, and 2.27 cmHz1/2/W, respectively.

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

Introduction

Infrared (IR) detectors are broadly classified into photon detectors and thermal detectors. Photon detectors are fast and more sensitive compared to the thermal detectors. As a result, these find applications in expensive weapon platforms, in astronomical observation instruments, or in special medical instruments where performance is the main concern. On the other hand, the emergence of uncooled detectors has opened new opportunities for IR detection for both military and commercial applications due to their small size, less power consumption, and lower cost making these the ideal choice for applications requiring high unit numbers with relatively lower performance. The key factor in developing a highly sensitive detector is to develop a thermometer material compatible with silicon technology to achieve high thermal isolation in the smallest possible area. [5] Bolometer IR detectors detect the changes of electrical resistance of thermally isolated materials due to the temperature change caused by the incident IR signal. The bolometer IR detectors studied, mainly the resistive type, were those that detected changes in the resistance of metal, semiconductor and superconductor materials. Bolometer IR detectors are characterized by simple manufacturing processes and are capable of operating at room temperatures. Recently, the bolometer IR detectors using titanium, vanadium oxide, and $YBa_2Cu_3O_{7-x}$ (YBCO) thin films have been studied for potential applications [6 ~ 8]. However, titanium thin films, which have the temperature coefficient of resistance of 0.28%/K, show a low sensitivity performance for the incident IR. Vanadium oxide thin films, with a single composition, are difficult to produce by the sputtering or implantation methods, because of compositional instability [9]. But YBCO, known as a high temperature superconductor, have shown various optical and electronic properties based on its oxygen content. For $x \approx 1$, YBCO possesses an orthorhombic crystal structure and exhibits metallic conductivity. As x is decreased to 0.5, the crystal undergoes a phase transition to a tetragonal structure and it exhibits semiconducting conductivity characteristics. As x is decreased further below 0.3, YBCO becomes a Hubbard insulator with a well defined energy gap in the order of 1.5 eV [10]. Semiconducting thin film, YBCO possesses a high pyroelectric coefficient at room temperatures, two hundred times greater than other thin film materials. YBCO films are characterized by the temperature coefficient of resistance in the range of 3.5 ~ 4%/K and low leakage current densities. Therefore, YBCO films are suitable materials for such applications as bolometer IR detectors [11 ~ 12].

In this study, semiconducting YBCO thin films were prepared using the sol-gel method, method and were spin-coated in the SiO_2/Si substrate using YBCO

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alkoxide solutions. We have also investigated the structural and electrical properties of YBCO thin films with variation of oxygen partial pressure 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 [$Ba(OH)_2 8H_2O$], solvent propionic acid, and propylamine. The stoichiometric molar ratio of yttrium acetate, barium hydroxide, and copper acetate was 1 : 2 : 3. 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. The YBCO films were air dried at 200 ~ 250 °C for several minutes. Because one coating generally gives a thickness of 0.06 ~ 0.08 μm, the 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 hr to remove the organic materials, and annealed at 650 ~ 800 °C for 1 hr in various oxygen partial pressures to crystallize it into a tetragonal structure. The crystalline structures of the YBCO thin films were analyzed by X-ray diffraction (XRD) with CuKa radiation. 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 an 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 due to the variation of oxygen partial pressure. All YBCO films showed $YBa_2Cu_3O_{7-x}$ phase and tetragonal structure. YBCO films Ar/O_2 at 9 : 1 and 8 : 2 showed the second phase such as $BaCuO_2$, BaY_2O_4 and $CuYO_2$. The oxygen content increased with the decrease the second phase such as. $BaCuO_2$, $CuYO_2$. The films Ar/O_2 at 7 : 3 showed the more obvious $YBa_2Cu_3O_{7-x}$ phase and a small second phase was observed. But, the Ar/O_2 at 6 : 4 showed 7 : 3 compared to less $YBa_2Cu_3O_{7-x}$ phase.

Fig. 2 shows the surface SEM micrographs of YBCO films due to the variation of oxygen partial pressure. The grain size increased with oxygen ratio, the YBCO film Ar/O_2 ratio at 7 : 3 showed an average grain size of about 50 nm. The YBCO films Ar/O_2 ratio at 9 : 1

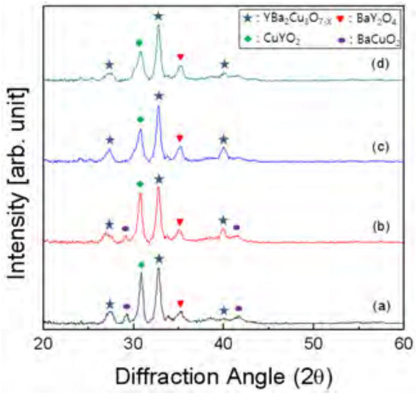

Fig. 1. XRD patterns of $YBa_2Cu_3O_{7-x}$ thin film as a function of oxygen partial pressure: (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4.

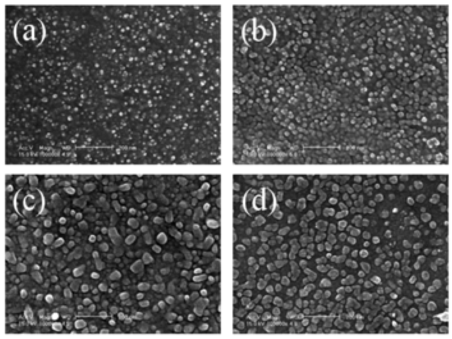

Fig. 2. Surface SEM micrographs of $YBa_2Cu_3O_{7-x}$ thin film as a function of oxygen partial pressure: (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4.

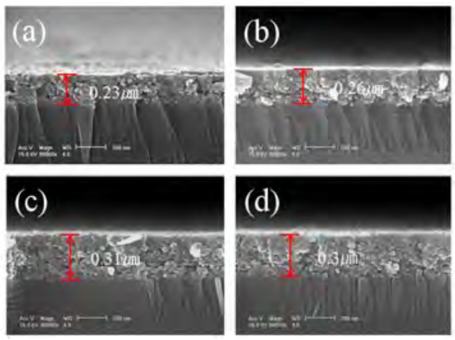

Fig. 3. Cross-sectional SEM micrographs of $YBa_2Cu_3O_{7-x}$ thin film as a function of oxygen partial pressure: (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4.

and 8 : 2 showed a small grain size due to the second phase. The film Ar/O_2 ratio at 6 : 4 showed a ratio of 7 : 3 compared to a less meticulous grain.

Fig. 3 shows the cross-sectional SEM micrographs of YBCO thin films due to the variation of oxygen partial pressure. The thickness of all the films was approximately 0.23 ~ 0.31 μm, and no dependence on oxygen partial pressure was observed. All films showed a relatively flat surface morphology and pore size distribution inside the films. Typically, the pores in the IR detector materials prevent the dispersion of the incident IR, and decrease the sensitivity of the IR detectors. Thus, to obtain good sensitivity properties, the films should have a dense, void free grain structure.

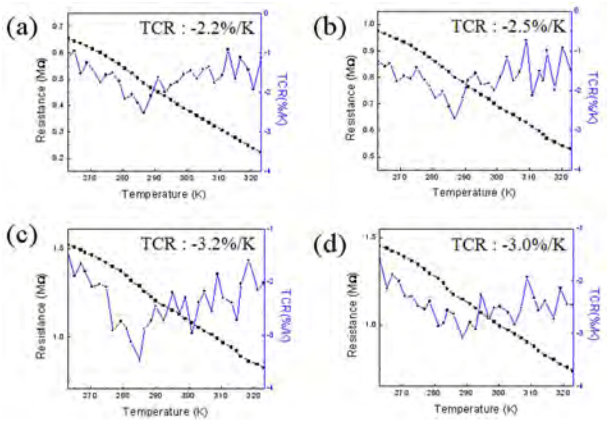

Fig. 4. Electrical resistance and TCR properties of $YBa_2Cu_3O_{7-x}$ thin film as a function of oxygen partial pressure: (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4.

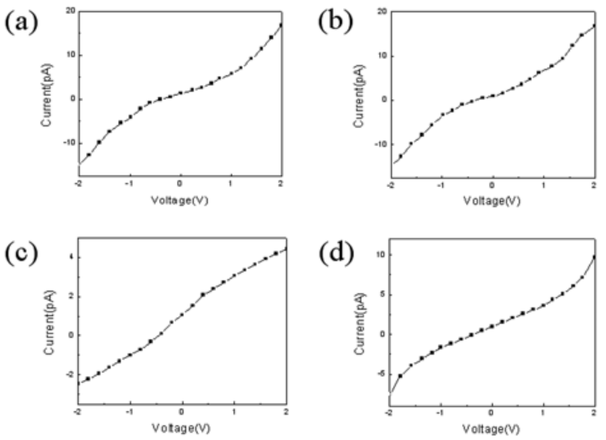

Fig. 5. I-V characteristics of $YBa_2Cu_3O_{7-x}$ thin film as a function of oxygen partial pressure: (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4.

Fig. 4 shows the temperature coefficient of resistance (TCR) of YBCO thin films with the variation of oxygen partial pressure. All YBCO films showed NTCR (negative temperature coefficient of resistance) properties, which means that the electrical resistance decreased with the increase in temperature of typical semiconductor materials. The electrical resistance and TCR increased with the increased oxygen ratio, and the YBCO films Ar/O_2 at 7 : 3 showed the highest values of 33 MΩ and -3.2%/K at room temperature This is because the grain size of single crystalline increased with the decrease the second phase, as shown in Fig. 2. However, the electrical resistance and TCR of films Ar/O_2 at 6 : 4, decreased due to less meticulous grain.

Fig. 5 I-V the characteristics of YBCO thin films in response to the variation of oxygen partial pressure. The current-voltage characteristics of the bolometer show a linear graph. Likewise the current-voltage characteristics of YBCO thin films show a linear graph. All YBCO films showed the Ohmic conduction properties, however, the slope of curves I-V changed proportionately to the changes in the applied voltage. This property may be understood in terms of the effect

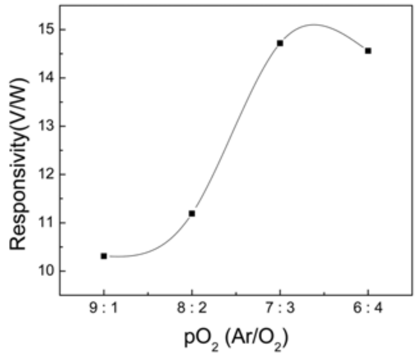

Fig. 6. Responsivity of $YBa_2Cu_3O_{7-x}$ thin films with variation of oxygen partial pressure.

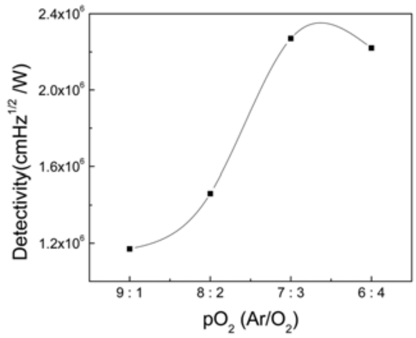

Fig. 7. Detectivity of $YBa_2Cu_3O_{7-x}$ thin films with variation of oxygen partial pressure.

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

of the difference of the work function between the semiconducting YBCO film and Ag electrode.

Considering the alignment between the incident light and the device, the blackbody furnace temperature of 600 K was used to measure the pyroelectric characteristics of YBCO films. Fig. 6 and 7 show the voltage responsivity and detectivity of YBCO thin films with the variation of oxygen partial pressure. The voltage responsivity, R_v that is, the ratio of the output voltage induced by the pyroelectric effect to the incident radiant power was calculated using eq. (1).

$$R = \frac{V_S}{EA_D}[V/W] \tag{1}$$

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*, that is, the signal-to-noise ratio of the detector when an incident infrared beam is radiated per unit area, was calculated using eq. (2).

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

Table.1 shows measuring parameters of responsivity and detectivity.

Conclusions

In this study, we fabricated the semiconducting YBCO thin film using the spin coating method. The YBCO thin films were annealed according to the variation of oxygen partial pressure. All YBCO films showed $YBa_2Cu_3O_{7-x}$ phase and tetragonal structure. The films Ar/ O_2 at 7 : 3 showed a more obvious $YBa_2Cu_3O_{7-x}$ phase, and a small second phase was observed. All YBCO films showed Ohmic conduction propertie. Temperature resistance coefficient, responsivity, and detectivity of the YBCO film sintered at 750 °C were 3.2%/K at room temperature, 14.72 V/W, and 2.27 × 106 cmHz1/2/W, respectively.

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