High T_c superconductors as NO_x and CO_x sensor materials

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The response of several ceramic oxide high T_c superconductors to NO_x and CO_x in Taguchi-type sensors has been investigated. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ decomposes in the presence of NO . $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-x}$ has sensitivity to CO and no sensitivity to NO_x . $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ show high selectivity against CO and CO_2 . They are promising materials for Taguchi-type NO_x sensors, the latter exhibiting the better response properties.

1. Introduction

The gas-detection concept of the Taguchi-type [1] NO_x sensor is based on chemisorption and/or catalytic activity at the semiconductor surface, i.e. by monitoring the resistance changes of a thin-film semiconductor caused by the electronic transfer between semiconductor adsorbent and chemisorbed gas.

SnO_2 and other metal oxides such as In_2O_3 and ZnO modified SnO_2 have been investigated as NO_x sensor materials for many years [2–7]. V_2O_5 and its modifications show high sensitivity [8–10]. ATiO_3 ($A = \text{Al, Nb, Ta, Sb, As, Ga, In, Sc, Mg, Y, Pb, Ca, Sr, Cd, Zn, La}$ and Ba) have been investigated as NO_x sensor materials [11]. $\alpha\text{-Fe}(\text{OOH})$, $\gamma\text{-Fe}(\text{OOH})$, and amorphous $\text{Fe}(\text{III})$ hydroxide exhibit low-temperature sensitivity for NO_x [12]. In recent years, phthalocyanine is broadly studied for use as trace- NO_x sensors [13–15].

Several ceramic high T_c superconductors exhibit high catalytic activity for NO_x oxidation or reduction [16–22]. Göpel [23] has suggested that the members of this family are probable sensor materials. Schoonman [24] suggested that the oxide superconductors may be used as NO_x sensing materials.

In the present study, the NO_x and CO_x sensing behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-x}$,

$\text{BiSr}_2\text{CuO}_{6+x}$ (2201-phase) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (2212-phase) has been investigated.

2. Experimental

Thick films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were prepared by spraying aqueous solutions of $\text{Y}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ with $\text{Y}:\text{Ba}:\text{Cu} = 1:2:3$ on a single crystal ZrO_2 (001) as substrate, and heat treated according to the procedure for preparing bulk materials [25,26]. The structure is identified with X-ray diffraction as the orthorhombic phase.

The Nd-Ce-Cu-O pellet is prepared by solid state reaction according to Takagi et al. [27].

Thin films of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ were prepared from mixtures of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, SrCO_3 , CaCO_3 and $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ with a molar ratio of $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 2:2:1:2$. Thoroughly ground mixtures were pre-reacted at 820°C in air for 20 h. The resulting products were ground and subsequently sintered at 850°C in air for about 20 h. The sintered materials were then ground in a ball-mill to a particle size of 1–10 μm in diameter. These powders were distributed homogeneously on Al_2O_3 substrates which had been cleaned in acetone. The amount of powder was chosen so as to obtain films with thickness of less than 100 μm . Subsequently, the particles on the substrates were melted at 950°C for 8 to 10 min. The film was polished to a thickness of about 20–30 μm .

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These films were then annealed at 850°C in air for 20 h.

Thick films of $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ were prepared by a similar method but with short annealing times. In addition, thin films of $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ were obtained with Electron Beam (EB) evaporation, using a Bio-Rad Turbo Coater. The structure of the films was identified by X-ray diffraction. The 2201-phase was obtained.

The electrical resistance of the materials was measured using a standard four-probe measurement. The samples were exposed to different NO_x or CO_x containing ambients in a test cell. The sensitivity and selectivity of the materials to NO, NO_2 against CO and CO_2 were studied at different temperatures.

3. Results and discussion

The sensitivity, S , of the samples to the various gases is defined as

$$S = R/R_0, \quad (1)$$

where R denotes the resistance of the sample on exposure to NO or other gases while R_0 is the resistance of the sample in air as a reference.

The flow rate of gases in our experiments is 200 ml/min. Usually, the response is influenced by the flow rate. An account of this parameter will be reported at a later stage [28].

3.1. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thick film

Fig. 1 shows the resistivity change when exposed to 500 ppm NO in air. The data suggest a diffusion-controlled process, which is consistent with early reports that this material can absorb large amounts of NO and eventually decomposes. This process is not reversible [16]. Hence, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is not a suitable material for utilization in NO_x sensors.

3.2. $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-x}$

At 294°C, this material does not show any resistivity change when exposed to NO_x . For 500 ppm CO in air, S has the value 0.97. At 401°C, no sensitivity to NO_x and CO_x could be measured.

Fig. 1. Time dependence of the resistivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in 500 ppm NO in air at 301.5°C.

$\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-x}$ is also not a suitable material for utilization in NO_x sensors.

3.3. $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ (2201-phase)

Fig. 2 presents the response behaviour of $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$. Its upper limit is lower than that of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. The base line of the signal can be recovered when the materials are exposed to air again.

Fig. 3 presents the results of the response of a $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ thin film prepared by electron beam evaporation using single phase material as source, and annealed at 800°C for 10 min with subsequent cooling in the furnace to 600°C and kept at this temperature for 20 h. In the case of the present thick films, it is seen from SEM pictures that the films are

Fig. 2. The temperature dependence of the sensitivity of a thick film $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ to NO.

Fig. 3. The temperature dependence of the sensitivity of a $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ thin film (EB) to NO.

Fig. 5. The temperature dependence of the sensitivity of a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ thick film to NO.

Fig. 4. The temperature dependence of the sensitivity of a thick film of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ to NO, NO_2 , CO and CO_2 .

composed of grains and that the width of the necks is much larger than the Debye length which is normally 100 Å [28]. The resistance is "bulk-trap-limited" [29]. It is consistent with the work reported by Xu et al. [30,31] which reveals that the sensitivity can be enhanced by reducing the grain size.

3.4. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (2212-phase)

Fig. 4 shows the temperature dependence of the sensitivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ to NO, NO_2 , CO and CO_2 . The optimal temperature is 350°C. The sensitivity of a thick film to 500 ppm NO was much higher than that to 500 ppm CO and 1% CO_2 at 350°C. The sensitivity to NO_2 is lower than that to NO but exceeds that to CO. Therefore, this 2212-

phase is sensitive and selective enough for NO detection. The sensitivity of a thick film of the 2212-phase is plotted as a function of NO in fig. 5.

4. Conclusions

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ reacts with NO and decomposes. $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-x}$ has no selectivity against CO. Both materials are not suitable NO_x sensing materials. $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ exhibit good stability, reproducibility and high selectivity against CO and CO_2 . They are candidate materials for Taguchi-type NO_x sensors. The latter material exhibits the best response behaviour. It is assumed that the sensitivity of the Bi-based materials can be improved further by using films having smaller grain sizes.

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