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Ethanol sensing properties of $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ films at low operating temperatures

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Abstract: $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNdT) films were deposited on $Pt/Ti/SiO_2/Si(100)$ substrates by a metal organic decomposition (MOD) method, and annealed by a rapid thermal annealing process in oxygen atmosphere and in air, respectively. The crystalline structures and morphologies of BNdT films were characterized by X-ray diffraction and field-emission scanning electron microscopy, and the gas sensing properties were measured by monitoring its resistance at different gas concentrations. The results indicate that the BNdT films annealed in air are of porous microstructure and rough surface, and the annealing atmosphere has great influence on gas sensing properties. At an operating temperature of 100 °C, the BNdT films annealed in air are of high response value to 1×10^{-6} gaseous ethanol, and the detecting limit is as low as 0.1×10^{-6}. The corresponding response and recovery time is about 10 and 6 s, respectively. The results can offer useful guidelines for fabricating high performance ethanol sensors.
Key words: BNdT film; ethanol sensing properties; metal organic decomposition; annealing atmosphere; low operating temperature

1 Introduction

In recent years, perovskite-structured compounds (general formula ABO_3) have been attracted much attention due to their unique catalytic action [1], piezo-electric properties [2,3], and special performance in gas sensors [4−6]. Perovskite ABO_3 oxides, an important material family for the electronic and information technology, are also promising candidates for gas sensors [7]. Compared with simple metallic oxides, perovskite oxides are more stable and reliable [8]. In addition, the perovskite structure has two different sized cations, which makes it amenable to a variety of dopant additions. This doping flexibility allows for control of the transport and catalytic properties to optimize sensor performance for particular applications [9]. The ABO_3-type oxide materials of rare-earth elements are highly defective and have oxygen deficient structures, in which the valence state of metal ions may be controlled by temperature, oxygen partial pressure and dopants [3,10,11]. Their sensitive and selective characteristics can be controlled by selecting suitable A and B atoms or chemical dopants to give $A_{1-x}A'_xB_{1-y}B'_yO_3$ materials [12−15]. Hence, the ABO_3-type oxide materials with special structures and morphologies have received considerable attention due to their special performance in gas sensors [16,17]. As can be foreseen, integrative devices with various applications will be vital for the next generation of electrical devices with more powerful functions and much smaller size [17]. For instance, TiO_2 may be chosen for fabricating photoelectric-gas sensors with special performance [18−20].

Up till now, the gas sensing materials worked at low temperature are favourable for fabricating low power consumption sensors, and several approaches are often used to lower the operating temperature of the gas sensing materials. One example is to add noble metal catalyst to the surface of the sensing materials [21,22]. The other is to reduce the diameter of the sensing materials, making it close to or smaller than the space-charge length (L_d) [23−26]. Hence, the current research mainly focuses on the development of reduced-temperature operation of the gas sensors for their further industrial applications. $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNdT) thin film, as a good ferroelectric and

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piezoelectric material, has been widely investigated for their large remnant polarization ($2P_r$) and low leakage current [27−29]. However, relatively few reports for the gas sensing properties of BNdT thin film are available in the literatures. In this work, the ethanol sensing properties of BNdT thin films synthesized by metal organic decomposition (MOD) are investigated by exposing them to gaseous ethanol at different temperatures and concentrations. It is worth mentioning that this research may offer useful guidelines for the further industrial applications in fabricating high performance and low power consumption gas sensors.

2 Experimental

The BNdT films were fabricated on $Pt/Ti/SiO_2/Si$ (100) substrates by metal organic decomposition (MOD). During the spin-coating procedure, the precursor solution for coating was prepared by dissolving bismuth nitrate, neodymium nitrate and titanium butoxide in proportion in glacial acetic acid at room temperature, with appropriate amount of acetylacetone added to stabilize the solution. 10% excess amount of bismuth nitrate was added to compensate for possible bismuth loss during annealing. The final concentration of precursor solution was 0.1 mol/L in BNdT, and the mix solution was spin-coated on substrate at 4000 r/min for 40 s. After the spin-coating procedure, the films were dried at 180 °C for 3 min, and pre-fired at 400 °C for 3 min to remove residual organic compounds. To investigate the effect of annealing atmosphere, the coated BNdT films were annealed by a rapid thermal annealing process for 10 min in oxygen atmosphere (BNdT-1) and in air (BNdT-2) at temperature of 750 °C, respectively. The crystalline structures of BNdT films were characterized by using a D/max 2500VK/PC X-ray diffraction (XRD) with Cu K_α radiation (λ=1.5405 Å), and the morphologies of BNdT films were recorded by FEI Quanta FEG 450 field emission scanning electron microscopy (FE-SEM).

Ethanol sensing characteristics were performed on a CGS-1TP intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd., China), and the schematic diagram of measure setup is shown in Fig. 1. The analysis system offers an external temperature control (from room temperature to 500 °C). The BNdT films with $Pt/Ti/SiO_2/Si$ (100) substrates were placed on the temperature control and pre-heated at different operating temperatures for about 30 min. Two probes were pressed on the surface of BNdT films with $Pt/Ti/SiO_2/Si$ (100) substrates by controlling the position adjustment in the analysis system. When the electrical signal is stable, ethanol gas is injected into the test chamber (18 L in volume) by a DGD-III dynamic gas distribution system (Beijing Elite Tech Co., Ltd., China). After the resistance reached a new constant value, the test chamber was opened to recover the BNdT films in air. The resistance and response were collected and analyzed by the system in real time.

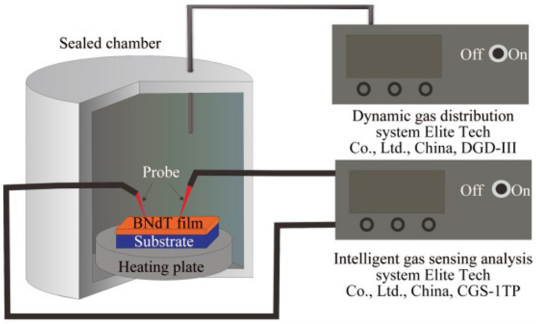

Fig. 1 Schematic diagram of measure setup

The response value (S) is designated as $S=R_a/R_g$, where R_a is the BNdT films resistance in air (base resistance) and R_g is its resistance in a mixture of ethanol gas and air. The time taken by the resistance to change from R_a to $R_a-90\%(R_a-R_g)$ is defined as response time when the ethanol gas is introduced to the BNdT films, and the time taken from R_g to $R_g+90\%(R_a-R_g)$ is defined as recovery time when the ambience is replaced by air.

3 Results and discussion

The XRD patterns of BNdT-1 and BNdT-2 are shown in Fig. 2. The peaks are indexed according to the standard diffraction pattern data of perovskite $Bi_4Ti_3O_{12}$ phase (JCPDS No. 73−2181). It is observed that all peaks of BNdT films coincided with those of $Bi_4Ti_3O_{12}$ films without any second phases. The BNdT-1 and BNdT-2 films consisting of a single phase of bismuth-layered perovskite are polycrystalline, without a preferred orientation, and both of them have good crystallinities. It is evident that the Nd^{3+} substitution does not affect the bismuth-layered structure of $Bi_4Ti_3O_{12}$ [30].

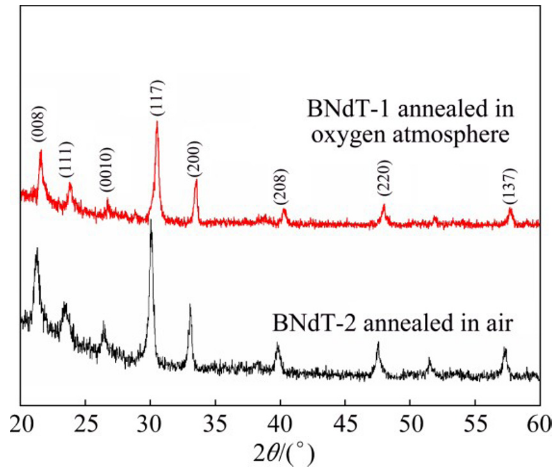

Fig. 2 XRD patterns of BNdT-1 and BNdT-2