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稀土氧化物掺杂对 SnO_2 基气体传感器材料性能的影响

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摘 要 采用化学共沉淀法制备 Y_2O_3, ZrO_2, Er_2O_3 和 Sb_2O_3 掺杂 SnO_2 基气体传感器. 结果表明掺杂后的材料经煅烧后, 平均晶粒尺寸均小于 30nm, 比未经掺杂的材料小. 将各掺杂体系不同成分材料制备成厚膜传感器, 进行了对 CO 气体敏感度性能测试, 发现掺杂稀土氧化物的气体敏感度较纯 SnO_2 厚膜传感器高. 其中掺杂 Er_2O_3 材料性能最好.

关键词 稀土氧化物 纳米 传感器

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ROLE OF ADDITIVES IN SnO_2 BASED GAS SENSOR MATERIALS

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ABSTRACT Nanocrystalline SnO_2 powders doped with different metal oxides including Y_2O_3, ZrO_2, Er_2O_3 and Sb_2O_3 were synthesized by chemical co-precipitation method. The Y, Er and Zr–SnO_2 are new systems and have not been reported before. The influence of dopants on the crystallite size and electrical properties has been characterized. The results showed that SnO_2 powders doped with 3% ~5% (mass fraction) Y_2O_3 or Sb_2O_3 have smaller crystallite sizes than that of the undoped material. The crystallite sizes were less than 30nm while the calcination temperatures were up to 1050 ℃. Grain growth was significantly inhibited by the Sb doping. Measurements of electrical property for the doped sensors showed higher sensitivity to CO at 350 ℃ than the pure SnO_2 sensor. Among these doping oxide sensors, Er_2O_3 doped sensor had the highest sensitivity to CO gas.

KEY WORDS rare earth oxide, nanocrystalline, sensor

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1. Introduction

Tin dioxide (SnO_2) based gas sensors exhibit high sensitivity to various reducing/oxidizing gases. Considerable attention has recently been focused on the development of solid state gas sensors based on films with crystallite size smaller than Debye length of electrons in the material, which showed an increased gas sensitivity and short response time [1~4]. In general, the factors that affect the crystallite size of the SnO_2 based gas sensor materials are fabrication methods, heat treatment conditions and compositions. Doping is an effective way to control the crystallite size. By using suitable dopants, such as Pd, Pt, Al_2O_3, CuO, Sb_2O_3, MgO, and SiO_2, the sensitivity and selectivity of a sensor could be remarkably improved[2,5~10]. The additives improved the gas sensitivity and selectivity of a sensor in two ways: either to limit the grain growth, or to reduce the intrinsic Debye length. Studies indicated that if trivalent ions were doped partially into the SnO_2, the electrical carrier concentration would decrease, so that the Debye length of SnO_2 would increases. On the contrary, pentavalent dopants would bring about a smaller Debye length, thus reduce the sensitivity[5]. The behavior of different valence doping in SnO_2 matrix was investigated in this paper. The selected dopants were Sb_2O_3, Y_2O_3, Er_2O_3 and ZrO_2.

2. Experiment

Tin oxide–based powders were prepared by solution co–precipitation method. The thick films for electrical property measurements were prepared using screen print technique. The measurement of gas sensitivity was carried out in a quartz tube with built–in heater and electrodes. The gas concentration was controlled by a flowmeter. The resistance was measured by using four–point–probe method. The sensitivity of the sensor was defined as R_a/R_g, where R_a was the resistance of the sensor in air and R_g was the resistance during exposure to the testing gas. X–ray diffraction was performed on Rigaku rotating anode diffractometer using Cu K_α radiation.

3. Result and Discussion

3.1 Effect of doping on crystallite size

Fig.1 indicated that the powders used in the experiment were crystalline with tetragonal rutile structure in the temperature range from 450 ℃ to 1050 ℃. The peak width became narrow with the increase of temperature, which means the crystallite size became large as temperature increased. Fig.1 also revealed the appearance of cubic yttria peak at 1050 ℃. This result showed that the doping limit or solubility of yttria in SnO_2 was less than 3% (mass fraction). In the it was, in general, that the solubility will increase with the increase view of

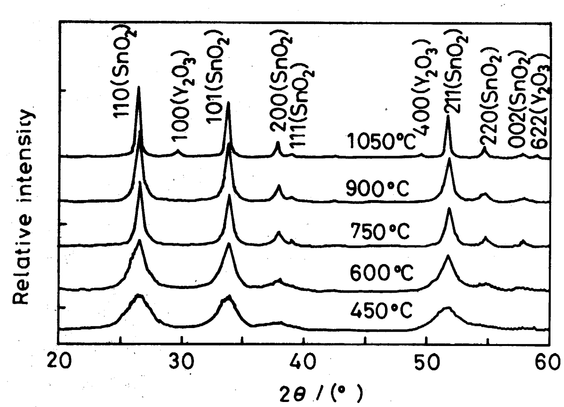

Fig.1 X–ray diffraction patterns of 3% Y–SnO_2 powders calcinated at different temperatures

solid phasediagram, of temperature, and thus the yttria peaks will be supposed to appear at low temperature. The result in Fig.1 seemed in contradiction to that point. In fact, the yttria peaks existed at low temperatures. They became very weak or invisible due to the very fine crystallite size resulted from lower temperature calcination. In order to make sure on peak width change and phase evolution versus temperature, a pellet of this composition was prepared using cold isostatic press method and fired at 1500 ℃ for 3h. The results showed the intensity of the second phase peak has a big increase and the second phase changed from cubic Y_2O_3 to cubic $Y_2Sn_2O_7$ (Fig.2). From this point, a way to evaluate the doping limit was provided, i.e., it should check the powder calcinated at high temperature.

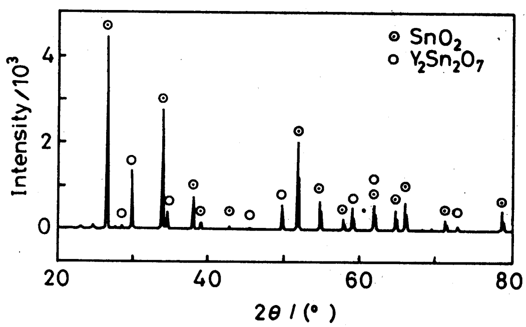

Fig.2 X-ray diffraction patterns of 3% Y-SnO_2 pellet sintered at 1050 ℃ for 3h

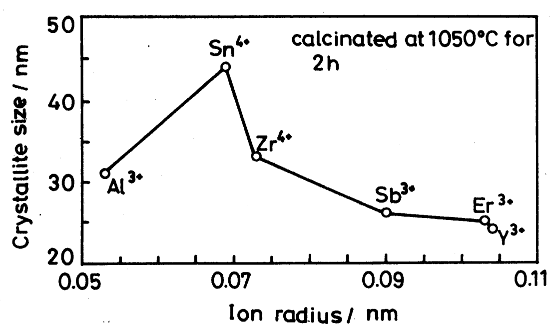

Fig.3 Relationship between SnO_2 crystallite size and ion radii of dopants

The average crystallite size, D, was estimated by the Debye–Scherrer formula using the full–width–at–half–maximum, which was after the correction for instrumental broadening. From Fig.3, the crystallite size decreases with the increase of $|r_d - r_{Sn}|$, here r_d was the ionic radius of the dopant, r_{Sn}, the ionic radius of Sn. Y ion had a bigger radius, so it had a smaller solubility in SnO_2 lattice, and the excess content simply acted as a stabilizer of the SnO_2 crystallites, therefore, Y doped SnO_2 in this studies showed the smallest crystallite size. Here, it is emphasized that the crystallite sizes were the average of compositions of 1%∼5% for Y–, Sb– and Zr–SnO_2 (the data for Al doped SnO_2 after reference[5]).

3.2 Effect of doping on sensitivity

The effects of additives on the gas sensitivity to CO were examined. The typical relationships between resistance and CO concentration for 3% Er_2O_3 doped tin dioxide thick film sensor materials were shown in Fig.4. The sensitivity of sensors of different metal oxides was shown in Fig.5, here the sensitivity was defined as R_a/R_g, where R_a is the resistance of the sensor in air and R_g is the resistance during exposure to the test gas. The 3% Er_2O_3, Y_2O_3, Sb_2O_3 and ZrO_2–doped sensors showed increase in sensitivity as compared with pure SnO_2 sensor. With the increase of the CO concentration, the sensitivities of doped sensors increased fast while pure SnO_2 only had a slight increase from 2×10^{-4} to 7×10^{-4} by volume. Among them, the 3% Er_2O_3–doped SnO_2 had the highest sensitivity in the whole gas concentration measuring range. At 7×10^{-4}, both Y_2O_3 and

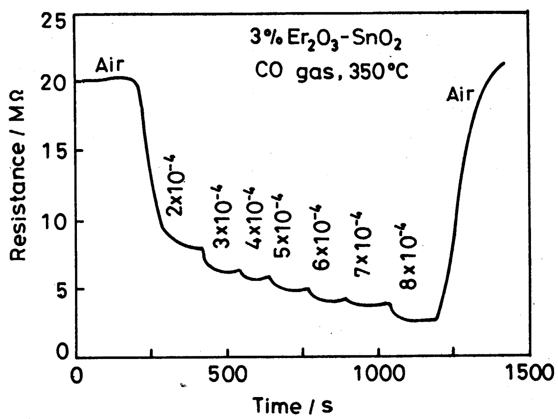

Fig.4 Resistance *vs* CO concentration for 3% Er_2O_3–SnO_2

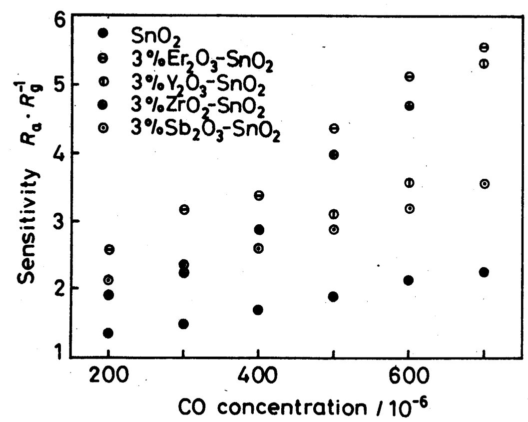

Fig.5 Sensitivity as a function of CO concentration at 350 ℃ for various doping materials

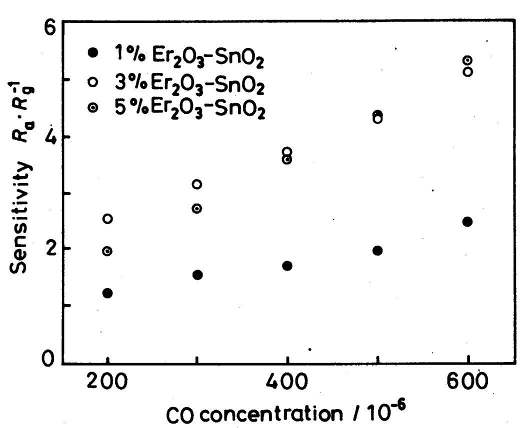

Fig.6 Sensitivity as a function of different erbium oxide contents in SnO_2 matrix

Er_2O_3 doped sensors exhibit higher sensitivity values. This may be due to the microstructure changes induced by large ironic radius difference between doped ions and tin ion. Here, the Er ion radius is 0.103 nm, Y ion, 0.104 nm, while Sn ion, 0.069 nm. The difference was over 30%. For the other two doped ions, Zr ion and Sb ion, the difference was less than 30%. It was emphasized that all the sensors used in experiments (pure and doped) have similar crystallite size, therefore the difference in sensitivity might be chiefly due to the difference between ion radius. In addition, the special electron structure of rare earth ions also plays a part role on the sensitivity. The electronic interaction of SnO_2 associated with the 4f electrons in Er ion may induce a shift in binding energy of Sn 3d and O1s electrons to a lower energy. The shift will result in the increase of sensitivity[11]. However, rare earth ions not only affect the microstructure, but also affect the Debye length. Different contents of rare earth ion doping were checked. Fig.6 showed the gas sensitivity as a function of erbium oxide content in tin dioxide matrix, this study demonstrated that doping with 3%~5 % has the strong contribution to sensitivity.

4. Conclusions

The additions of yttrium and antimony oxides in tin dioxide by solution coprecipitation method can limit the grain growth, especially at higher calcination temperatures. SnO_2 doped with 3% Y_2O_3, Er_2O_3, ZrO_2 and Sb_2O_3 have higher sensitivity to CO at 350 ℃ than the pure SnO_2. Among these doping oxide sensors, Er_2O_3 doped sensor has the highest sensitivity to CO.

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