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Ethanol Sensing Performances of Zinc-doped Copper Oxide Nano-crystallite Layers

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The synthesis via chemical solutions (aqueous) (SCS) wet route is a low-temperature and cost-effective growth technique of high crystalline quality oxide semiconductors films. Here we report on morphology, chemical composition, structure and ethanol sensing performances of a device prototype based on zinc-doped copper oxide nanocrystallite layer. By thermal annealing in electrical furnace for 30 min at temperatures higher than 550 ˚C, as-deposited zinc doped Cu_2O samples are converted to tenorite, $Zn_xCu_{1-x}O_y$, (x=1.3wt%) that demonstrate higher ethanol response than sensor structures based on samples treated at 450 ˚C. In case of the specimens after post-growth treatment at 650 ˚C was found an ethanol gas response of about 79 % and 91 % to concentrations of 100 ppm and 500 ppm, respectively, at operating temperature of 400 ˚C in air.

Keywords: Chemical synthesis, nanocrystalline, ethanol, film, copper oxide, Cu_2O.

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1. INTRODUCTION

Ethanol (EtOH), that is also known as ethyl alcohol, is a colorless, flammable, volatile liquid and is extensively utilized in pharmacology, cosmetic production, chemical and food industry, especially in breath analysis and wine-quality monitoring. Ethanol can be used as a fuel for motor vehicles, thus it is an important alternative fuel that produces less greenhouse emission compared to other conventional fuels like methane, propane, etc. Moreover, ethanol consumption is one of the major causes of traffic accidents [1]. In this context appear necessities for monitoring of ethanol vapors to offer safety in homes, vehicles, industry and for detection of the blood alcohol level (BAC) in the body of the drivers [1]. Conventional ethanol sensors are based on oxide semiconductors and are widely used in this domain due to their exceptional properties at nanoscale range, that offer high response, long life cycle, good selectivity, robustness and low cost. Many research activities have been done in the field of ethanol sensors based on oxide semiconductors. One of the most popular among them are *n*-type oxide semiconductors like ZnO [2], SnO_2 [3], WO_3 [4], etc. On the other hand, *p*-type oxide semiconductors like CuO, Cu_2O, NiO, Cr_2O_3, Co_3O_4, etc. have received relatively less attention.

Cuprous oxide (Cu_2O) has been widely studied as a promising material for conversion of the solar energy due to its nontoxicity, low-cost and relatively simple synthesis process [5]. But there are several reports on the ethanol sensing of Cu_2O based sensors with different structures such as combo-like nanorods [6], unifaceted crystals [7], etc. On the other side, cupric oxide (CuO) is known to be an important material in fabrication of high-temperature superconductors [8]. Many researchers have reported that CuO nanostructured films have higher gas response than those of Cu_2O [9]. Thus, it is of practical interest to investigate influence on ethanol gas response of such parameters, like temperature of thermal treatment and operating temperature of device in case of doping of copper oxide films. Generally, there are only few reports on doped copper oxide based sensors, on Zn-doped CuO in particular are less. A motivation of our research were previous promising results proving that by doping CuO nanorods with Cr it was possible to obtain good selectivity to NO_2 gas [10]. Hübner et. al. has reported that gas response of sensors based on the *p*-type oxide semiconductors is lower than for *n*-type based ones and is equal to the square root of gas response for sensor based on *n*-type oxide semiconductors [11]. Thus, according to previous papers it is more difficult to obtain a *p*-type oxide semiconductor based sensor with a high response.

In current report, we present experimental data on as-grown Zn-doped Cu_2O nanocrystalline films, which were subject of post-growth thermal annealing (TA) in electrical furnace and changed from cuprite phase to cuprite/tenorite phase, then to tenorite crystal phase. Ethanol response of the specimens after different TA treatments and operating temperatures (OPT) was investigated and reported below.

2. EXPERIMENTAL

2.1 Growth of zinc-doped copper oxide nanostructured films

Glass substrates were used for growth of zinc-doped copper oxide nanostructured films by SCS method. The cleaning and synthesis process were reported in our previous work [12]. Thickness of the films is in range of 0.85-0.90 μm as measured in cross-sectional view in scanning electron microscope.

2.2 Characterization

The samples of zinc-doped copper oxide nanostructured films were analyzed using scanning electron microscopy (SEM) instrument Carl Zeiss (7 kV, 10 μA). The compositional analysis of the specimens was carried out by EDX analysis in combination with SEM. Crystallographic information was derived from X-ray powder

