Sensors and Actuators B 209 (2015) 252–257

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Humidity sensing properties of $K_{0.5}Na_{0.5}NbO_3$ powder synthesized by metal organic decomposition

Mengjiao Yuan, Yong Zhang*, Xuejun Zheng, Bin Jiang, Peiwen Li, Shuifeng Deng

School of Physics and Optoelectronics, Xiangtan University, Xiangtan 411105, PR China

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form
20 November 2014
Accepted 25 November 2014
Available online 3 December 2014

Keywords:
$K_{0.5}Na_{0.5}NbO_3$ powder
Humidity sensing properties
Dissipation factor
Complex impedance plots

ABSTRACT

$K_{0.5}Na_{0.5}NbO_3$ (KNN) powder is synthesized via a metal-organic decomposition (MOD) method and characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and energy dispersive spectrometer (EDS). A humidity sensor, which is consisted of five pairs of Ag—Pd interdigitated electrodes and an Al_2O_3 ceramic substrate, is fabricated by spin-coating the KNN powder on the substrate. The humidity sensing properties of the KNN humidity sensor are investigated at room temperature within the relative humidity (RH) range of 11–95%. The variations of the KNN humidity sensor impedance are about four orders of magnitude within the whole humidity range from 11% to 95% RH at the frequencies of 60 Hz and 100 Hz. The response time and recovery time of the KNN humidity sensor are all about 8 s and 18 s, and their maximum hystereses are all around 2% RH at 60 Hz and 100 Hz. Furthermore, at low RH and frequency conditions, the dielectric dissipation factor (DF) values of the KNN humidity sensor are small and hardly change, indicating that the KNN humidity sensor is of good insulating properties and reliability. The KNN powder is of broader potential applications for fabricating high performance humidity sensors.

1. Introduction

In recent years, measurement and controlling environmental humidity are of great importance in industry, agriculture, meteorology and human activities, and the humidity sensors have gained considerable attention [1–5]. More and more researchers are increasing paying their attention to exploitation of new materials in order to acquire humidity sensors with excellent properties such as linear response, higher sensitivity, wider humidity detection range and fast response speed [6–10]. Perovskite ABO_3-type complex metal oxides, an important material family for electronic and information technology, are also promising candidates for humidity sensors [2]. $K_{0.5}Na_{0.5}NbO_3$ (KNN) is a perovskite ABO_3-type complex metal oxide with the substitution of A-site ions. KNN is known to be a ceramic ferroelectric material with a higher Curie temperature [11–13]. KNN thin films have been widely studied because of their high Curie temperature and lead-free chemical composition [14–16]. KNN ceramics have also been recognized as promising piezoelectric materials for wide applications [16–18]. However, to the best of our knowledge, relatively few reports for the humidity sensing properties of KNN powder are available in the literatures.

The operating frequency is considered as an important parameter of humidity sensor by many researchers and it is generally about 100 Hz in previous work [19–22]. Zheng et al. reported the humidity sensing properties of A-site substituted Bi(Na, K)TiO_3 powder humidity sensor, and it was difficult to get the electric signal at the frequency under 100 Hz because of the high impedance [5]. Wang et al. reported that the impedance of the ZnO/TiO_2 humidity sensor was above 100 MΩ when the frequency was lower than 100 Hz, which was difficult to test [3]. Because of the appearance of skin effect in humidity sensing film at high frequency, the impedance of humidity sensor and the loss power are both increasing, which affect the humidity sensitivity and accuracy of humidity sensor [23,24]. Therefore, the low and wide working frequency range is benefit for the development of high performance humidity sensor.

Based on the previous researches [4,5,25,26], the humidity sensing properties of materials co-doped by K^+ and Na^+ are better than it only doped by K^+ or Na^+. In this paper, promoted by the distinct properties of KNN powder and its potential applications in humidity sensor, the KNN powder is synthesized by metal-organic decomposition (MOD) method, and the crystalline structures and morphologies of KNN powder are characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and energy dispersive spectrometer (EDS). The humidity sensor is

* Corresponding author. Tel.: +86 731 58292197.
E-mail address: zhangyong@xtu.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.snb.2014.11.118
0925-4005/

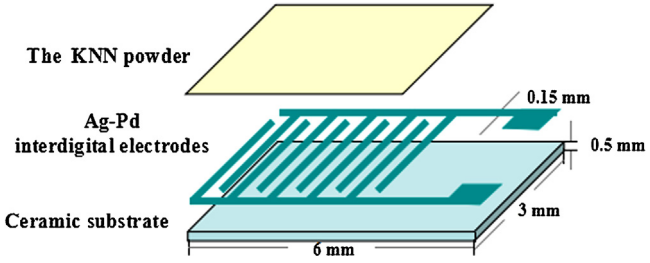

Fig. 1. A schematic diagram of the humidity sensor structure.

fabricated by coating the KNN powder on the substrate. The humidity sensing properties are investigated at different relative humidity (RH). We expect the results may offer useful guidelines to fabricate high performance humidity sensors which are of low and wide working frequency range.

2. Experimental details

2.1. Preparation and characterization of KNN powder

The KNN powder was synthesized by MOD method. The precursor solution was prepared by mixing potassium acetate, sodium acetate, and niobium ethoxide in 2-methoxyethanol solvent. In this case, 10 mol% excess amounts of K and Na alkoxides were added to compensate for their loss due to their volatility during heating [16]. And the final concentration of mixed solution was 0.30 mol/L. The above mixture was stirred for 12 h to promote the dissolution and reaction, and then kept for 12 h to gain the stable solution. The precursor solution was annealed at 650 °C for 3 h to obtain white powder. The powder was washed with deionized water and ethanol successively, and dried at 60 °C in air for further characterization. The crystalline structure of KNN powder was identified by XRD using a Bruker-AXS model D8-ADVANCE with Cu Kα ($\lambda = 0.15418$ nm). FE-SEM images were performed on a Carl Zeiss LEO1525 microscope with an accelerating voltage of 20 kV.

2.2. Fabrication and measurement of the humidity sensor

Fig. 1 shows a schematic diagram of the humidity sensor structure. The KNN powder was mixed with deionized water in a weight ratio of 100:25 to form a paste. The paste was spin-coated onto an Al_2O_3 ceramic substrate (6 mm × 3 mm, 0.5 mm in thick) with five pairs of Ag—Pd interdigitated electrodes (electrodes width and distance: 0.15 mm) to form a sensing film, and then the film was dried in air at 60 °C for 5 h. Finally, the humidity sensor based on KNN powder was obtained after aging at 95% RH with a voltage of 1 V, 100 Hz for 24 h to improve its stability and durability [27].

The humidity sensing properties of the KNN humidity sensor were measured on CHS-1 intelligent humidity sensitive analysis system (Beijing Elite Technology Co., Ltd.). The AC voltage applied was 1 V, and the frequency varied from 40 Hz to 100 kHz. The controlled humidity environments were achieved with supersaturation aqueous solutions of different salts in a closed glass vessel at room temperature, including LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3, which yielded 11, 33, 54, 75, 85 and 95% RH, respectively [28]. It took 10 h for the air in the glass vessel to reach equilibrium state in the investigations. The response time and recovery time were defined as the time taken by a sensor to achieve 90% of the total impedance change in the case of adsorption and desorption [29,30]. The hysteresis was measured by switching the humidity sensor between the chambers of 11%, 33%, 54%, 75%, 85% and 95% RH, and then shifting back. The RH of laboratory atmosphere was maintained at 25% RH by using an automatic drier. All of the sensing measurements were performed at a constant temperature of 25 °C.

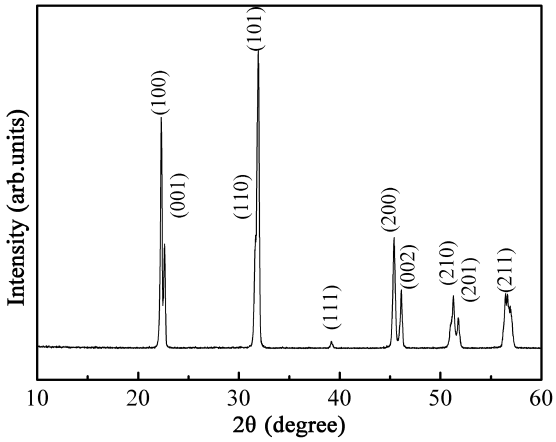

Fig. 2. XRD pattern of the KNN powder.

3. Results and discussion

3.1. Morphology and structure analysis

The crystalline structure of the powder obtained by sintering the KNN precursor solution is performed on XRD, and the XRD pattern is shown in Fig. 2. It can be noted that the XRD pattern reveals a single perovskite phase without any trace of secondary phase. The appearance of perovskite phase confirms that the homogeneous solid solution KNN is successfully formed [31], and the result of the XRD pattern is completely consistent with it of Sakamoto et al. [16]. In addition, the diffraction peaks are intensive and narrow which show that the powder obtained by sintering the KNN precursor solution is of good crystal quality [16,32,33].

The morphologies and composition of KNN powder are displayed in Fig. 3. It can be clearly seen that the KNN powder is of cuboid microstructure with diameters of 2–5 μm. Furthermore, as can be seen from Fig. 3(a), there are many fragments attached on the surface of each cuboid microstructure. The appearance of the fragments may be helpful for the increase of the specific surface, which may be quite useful for the water molecule adsorption and beneficial to its sensing properties. As shown in Fig. 3(b), the ratios of K/Na/Nb/O are approximately equal to the proportions of KNN, and the slight difference of element proportions is due to the volatilization of K^+ ion and Na^+ ion during the annealing process [34].

3.2. Humidity sensing properties

To find out the optimal relationship between impedance and RH of the humidity sensor based on KNN powder, the impedance vs. RH curves are measured at different frequencies (from 40 Hz to 100 kHz) and the results are shown in Fig. 4. We can see that the impedance of the KNN humidity sensor is obviously influenced by the frequency. The impedance decreases with increasing frequency in all RH range. The high humidity sensitivity and good linearity in the whole RH range are obtained when the frequency is 60 Hz and 100 Hz, and the impedance changes are about four orders of magnitude within the whole humidity range from 11% to 95% RH. At low RH, the impedance curves turn flat at high frequency, which indicates that the impedance of the KNN humidity sensor becomes independent of RH. This is because the electrical field direction changes fast at high frequencies and the polarization of water cannot catch up with it, resulting in the capacitance and