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Short communication

Effect of the seed layer on surface morphology and humidity sensing property of $CoTiO_3$ nanocrystalline film

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ABSTRACT

$CoTiO_3$ nanocrystalline film with enhanced humidity sensing property has been prepared via a two-step method. A nanostructured $CoTiO_3$ seed layer was firstly grown on silicate substrate by sol-gel process, and another $CoTiO_3$ layer was subsequently deposited on the seed layer by RF magnetron co-sputtering using TiO_2 and Co_2O_3 targets. The influence of seed layer on the microstructure and humidity sensing property of the $CoTiO_3$ film was investigated, it was found that the seed layer facilitates the intrinsic growth of $CoTiO_3$ grain and improves the crystallinity. Meanwhile, the surface morphology changes from brick-like grain type to a pebble-like pattern. The uniformity and alignment of the grains are both strongly related to the underneath $CoTiO_3$ seed layer. The as-prepared $CoTiO_3$ multilayer displayed enhanced humidity sensing properties such as the sensitivity to 95%RH reached to 41.9. The response time and recovery time was dramatically shortened, from 50 s for the seed layer to 5 s for the multilayer.

1. Introduction

Cobalt titanate, a p-type semiconductor with unique electronic and optical properties, has been regarded as a promising candidate for gas or humidity sensing material [1–7]. The existing $CoTiO_3$ sensors are generally ceramics sintered from fine powders or thick film devices [8–10]. However, study on $CoTiO_3$ thin film type sensor is relatively rare. He et al. [11] prepared a $CoTiO_3$ film by sol-gel method for humidity detection. The resistance decreased by a factor of 25 was registered over 11.3%RH~95%RH, with equilibration response times of 70 s~120 s. Yadav et al. [12] fabricated a nano-structured cobalt titanate thin film and found it shows good optical humidity sensitivity. In our previous work, $CoTiO_3$ thin film with (100)-preferred orientation was prepared by RF magnetron co-sputtering technique. This sputtered film exhibited ultra fast response to moisture due to the unique "fine-net" morphology and (100) orientation of $CoTiO_3$ [13]. Hence it is believed that the sensing property of $CoTiO_3$ film is closely related to its surface texture, preferred orientation as well as crystallization degree.

Recently, vertically aligned nanocrystalline film has attracted increasing attention due to the large surface area, suitable pore size distribution and effective pathway for gas and chargers transportation, thereby showing high sensitivity to humidity [14]. However, to our best knowledge, it still remains a great challenge to fabricate vertically oriented $CoTiO_3$ nanocrystalline film with controlled diameter, size distribution and high orientation consistency by RF magnetron sputtering. Herein, we design a two-step approach to modulate the surface configuration of $CoTiO_3$ film in order to improve the sensing ability. The preparation involves a pre-coating step of the seed layer and a subsequent sputtering process. The effect of the seed layer on the surface morphology evolution, as well as the improvement of the humidity sensing properties was discussed. This preparation of multilayers brings new possibility to tailor the structure and properties of $CoTiO_3$ film.

2. Experimental

The $CoTiO_3$ nanocrystalline film was prepared by RF magnetron sputtering on the prefabricated seed layer. Illustration of the two-step procedure is shown in Fig. 1(a). For preparing the $CoTiO_3$ seed layer (SL), the Si (100) substrate was dip-coated with a $CoTiO_3$ sol followed by annealing at 650 °C for 2 h in air. The precursor sol (pH=4.0) was composed of 0.02 mol L^{-1} $Co(NO_3)_2{\cdot}6H_2O$, 0.02 mol L^{-1} $Ti(OC_4H_9)_4$ and 0.02 mol L^{-1} ethylene diamine tetraacetic acid (EDTA). For more details, refer to the literature [7]. Then, an overlying $CoTiO_3$ film (RFL) was deposited by RF magnetron co-sputtering using two individual targets (Co_2O_3:TiO_2=100 W:400 W). The Ar pressure was 0.5 Pa and the sputtering duration was 1 h. Thereafter, the multilayer was

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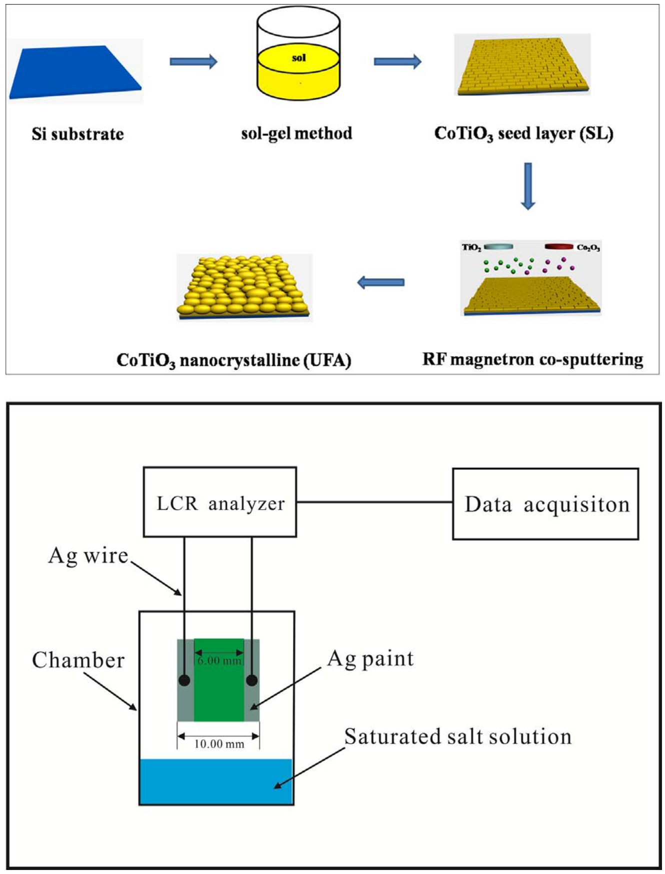

Fig. 1. (a) Schematic illustration of the two-step preparation of the UAF sample, (b) the humidity sensing measurement system.

annealed at 650 °C for 2 h again to produce the uniformly aligned $CoTiO_3$ nanocrystalline film (UAF). For comparison, the seed layer and the sputtered $CoTiO_3$ film were also prepared according to literature [7,13].

The humidity sensing behavior of the $CoTiO_3$ film is based on the resistance variation in different relative humidity (%RH) circumstances which were achieved by using supersaturated salt solutions [13]. The humidity sensitivity value (S) is calculated by Eq. (1):

$$S = \frac{R_{11\%}}{R_D} \tag{1}$$

where $R_{11\%}$ and R_D are the resistance taken at 11% RH and a detecting % RH. The response time and recovery time are defined as the time durations needed for a sensor to achieve 90% total resistance change in the case of adsorption and desorption, respectively. The experimental setup diagram is shown in Fig. 1(b).

The crystal structure and elemental composition were detected by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The surface morphology was characterized by atomic force microscopy (AFM).

3. Results and discussion

Fig. 2(a) shows the XRD patterns of the SL, RFL and UAF samples. The diffraction peak of the SL is assigned to a rhombohedral $CoTiO_3$. Obviously, the sharp and strong (211) peak is designated as the preferred orientation. Whereas, the RFL shows (100) plane preferred orientation. As for the UAF, the XRD pattern agrees very well with that given in JCPDS No.77-0153 of $CoTiO_3$. All the diffraction peak intensities were enhanced, particularly the (100) peak intensity increased dramatically, indicative of a crystalline quality improvement of the film. The UAF sample was further analyzed by XPS to ascertain the chemical composition, and the results are shown in Fig. 2(b)–(e). The sample survey implies Co, Ti, and O are the major components on the surface, and the calculated Co/Ti/O molar ratio is 1:1.2:3.8. The O1s peak can be deconvoluted into 2 peaks located at 529.1 and 531.4 eV, corresponding to the Co–O–Ti bonds [16] and the Ti–O bond [17]. The high-resolution XPS at the cobalt region shows 2p3/2 and 2p1/2 signals at 779.7 eV and 795.5 eV, while the 2p3/2 and 2p1/2 signals are at 458.0 eV and 463.8 eV of the titanium region, respectively. The splitting energy of 15.8 V between Co 2p3/2and Co 2p1/2, 5.8 eV between Ti 2p3/2and Ti 2p1/2 is typical value for Co^{2+} and Ti^{4+} [18].

Fig. 3 shows the AFM images of SL, RFL and UAF, the root mean square (RMS) roughness and thickness (T) of three films are presented as well. The $CoTiO_3$ seed layer shows a dense surface with the RMS value of 10.590 nm. The brick-like shape $CoTiO_3$grains are oriented perpendicularly to the substrate direction. When the seed layer was coated with a sputtered $CoTiO_3$ film, the uniformity and alignment of the grains were almost maintained. However, the grain size became larger, and the grain shape changed to a cobblestone style. The corresponding line profiles of these two films are shown in Fig. 3(d) and (e). Compared to the SL, the interstitial voids among the pebble-like shaped $CoTiO_3$ grains formed deeper pores with larger pore volume, indicating the UAF provides more adsorption sites and paths for water molecules and thus would facilitate the subsequently capillary condensation [15]. As for the RFL, a "fine-net" morphology was