Thin Solid Films 615 (2016) 427–436

Contents lists available at ScienceDirect

Thin Solid Films

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

Sol-gel derived oriented multilayer ZnO thin films with memristive response

Dawit Gemechu Ayana [a,*], Riccardo Ceccato [a], Cristian Collini [b], Leandro Lorenzelli [b], Valentina Prusakova [a], Sandra Dirè [a]

[a] Department of Industrial Engineering, University of Trento, via Sommarive 9, 38123 Trento, Italy
[b] FBK, BioMEMS, Via Sommarive 18, 38123 Trento, Italy

ARTICLE INFO

Article history:
Received 2 September 2015
Received in revised form 24 June 2016
Accepted 12 July 2016
Available online 14 July 2016

Keywords:
Zinc oxide
Sol-gel
Thin films
Preferential orientation
Memristive behavior

ABSTRACT

Sol-gel derived multi-layer ZnO films were prepared by spin coating technique on soda-lime glass, silica, silicon and platinum substrates from an alcoholic solution of zinc acetate dihydrate and monoethanolamine at different synthetic conditions. The curing and annealing conditions for the ZnO films were adjusted based on the study performed on the ZnO xerogel powders. Structural and morphological features as well as the thermal behavior of the samples were investigated by complementary techniques including electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric and differential thermal analyses, and X-ray diffraction analysis. According to the electrical measurements performed on ZnO thin films sandwiched between Pt/Ti/SiO_2 substrate and Ag dishes as a top electrode, the selected fabrication conditions were suitable for fulfilling the requirements of active resistive layers for the development of memristive devices.

1. Introduction

Memristor is the fourth fundamental passive circuit element in addition to resistor, capacitor and inductor, proposed by Chua as the missing electronic element in 1971 [1]. The predicted memristive behavior was found in Pt/TiO_2/Pt cell by Williams et al. in HP laboratory in 2008 [2] and opened perspectives for other inorganic oxides including zinc oxide [3]. ZnO is a well-studied low cost, non-toxic, wide band-gap (3.37 eV) luminescent semiconductor material [4,5] with high electron mobility, high thermal conductivity, large piezoelectric constants, large exciton binding energy (60 meV), and transparency of thin films [6]; thus, it offers many advantages over other metal oxide.

Due to the exceptional properties listed above, ZnO thin films have found the application in lasers [7–10], piezoelectric devices [11], light emitting diodes [12], surface acoustic wave devices [13], as electron transport layer in solar cells [14], thin film transistors [15] and sensors [16,17]. Different deposition techniques such as molecular beam epitaxy [18], sputter deposition [19], pulsed laser deposition [20], spray pyrolysis [21], chemical vapor deposition [22] and sol-gel processing [23] have been used to prepare ZnO thin films.

ZnO thin films for memristive devices were fabricated by several methods [24,25], contributing in altering properties of the semiconductor materials and significantly influencing the performance of the final device. Driven by the interest in chemical modification of ZnO semiconductor layer in a memristive cell, we recently reported preliminary results on the synthesis and characterization of ZnO thin films by the sol-gel process [26]. The proposed fabrication technique, i.e. sol-gel route, is a wet chemistry method in which molecular precursors transform into an oxide network through hydrolysis-condensation reactions. It has emerged as one of the most beneficial processing routes due to its advantages, including relatively low cost, easy processing and the ability to produce homogeneous films with different compositions at large deposition scale on a variety of substrates. It is widely used and recognized as an efficient fabrication technique for ZnO thin films [23] that allows tuning the synthetic parameters, including concentration and composition of the sol. Moreover, it is an effective process to fabricate multilayer, volatile free, dense and homogeneous ZnO thin films with controlled thickness and stoichiometry that are essential for the further development of the memristive cell. Thus, by optimizing both sol synthesis and coating preparation steps, the fine control over the desired properties of semiconductor film mentioned above can be achieved.

Inspired by the preliminary results reported in [26], a thorough investigation of sol's chemical composition influence on the properties of corresponding ZnO thin films was performed. Herein, a side-by-side analysis of ZnO thin films prepared from sols containing different amount of monoethanolamine is reported. In particular, the dependence of ZnO nanoparticle size and texture of the film from the chemical composition of the sol and nature of substrates is discussed. Additionally, the influence of processing conditions on the features of sol-gel derived layers is examined. In this paper, we present the complete study of the influence of processing conditions on the features of sol-gel derived ZnO thin films to be used as active resistive layers in

* Corresponding author.
E-mail address: dawitgemechu.ayana@unitn.it (D.G. Ayana).

http://dx.doi.org/10.1016/j.tsf.2016.07.025
0040-6090/

memristors. The preparation of sol-gel derived multi-layer ZnO thin films from different sol compositions was developed by spin coating of ZnO sol on soda-lime glass, silica, platinum and silicon substrates. The reported optimization of the processing parameters and synthesis conditions for ZnO thin films preparation was done based on the comprehensive characterization of thermal, morphological and structural properties of both xerogel powders and coatings. Finally, a corresponding memristive cell based on the refined ZnO thin films was fabricated.

2. Experimental part

Zinc acetate dihydrate (ZAD), monoethanolamine (MEA) and ethanol were purchased and used without further purification. ZnO sols were synthesized by dissolving ZAD ($Zn(CH_3COO)_2 \times 2H_2O$, Riedel-De-Haen, ≥99.5%, 1 kg) and MEA ($H_2NCH_2CH_2OH$, Sigma-Aldrich, 99%, 100 mL)) in ethanol (C_6H_6O, Sigma-Aldrich, ≥99.8%, 1 L), adjusting ZAD to MEA molar ratio (Table 1). The synthetic procedure was adopted from [27]. In a dry two-necked round-bottom flask, ZAD was dissolved in ethanol in 0.1 M concentration and MEA was added drop-wise; the mixture was stirred at 80 °C for 2 h and cooled down to room temperature under nitrogen to yield a clear and homogeneous solution.

2.1. ZnO xerogel powders preparation

ZnO xerogel powders were prepared by ZnO sol-casting on Petri dishes. After gelling and drying at RT in air, the powders were heated at 150 °C or 250 °C for 1 h, and finally annealed in air at 400 °C for 4 h. Fig. 1 shows the flow diagram for ZnO xerogel powders and films preparation by sol-gel process, using the spin coating deposition.

2.2. ZnO thin films preparation

Soda-lime glass, silica and silicon substrates were cleaned prior to ZnO sol deposition as previously reported [26]. Platinum (Pt(50 nm)/Ti(5 nm)/SiO_2) substrates were fabricated by electron beam evaporation of Ti (5 nm) and Pt (50 nm) on a double side polished Electric Fused Quartz wafer (650 μm) and used as a bottom electrode for the electrical measurements [28]. The engineered electrodes were brushed and rinsed with acetone, 2-propanol, and deionized water; and finally dried in oven at 80 °C for 1 h. Oxygen plasma etching was performed on the platinum substrates dried in N_2 stream prior to ZnO sol deposition in a clean room to increase adhesion between sol and Pt/Ti/SiO_2 electrode [28]. The substrates were used immediately after the cleaning and treatment procedures for ZnO sol deposition by spin coating technique (Fig. 1). For the ZnO thin films prepared in a clean room, fresh

Table 1
ZnO thin films prepared from [ZAD] = 0.1 M on different substrates.

Samples	ZAD:MEA	layers
Soda-Lime Glass		
G1-1.34	1:1.34	1
G4-1.34	1:1.34	4
G8-1.34	1:1.34	8
G8-0.5	1:0.5	8
Silica		
S8-1.34	1:1.34	8
S8-0.5	1:0.5	8
Si wafer		
Si8-1.34	1:1.34	8
Si4-0.5	1:0.5	4
Si8-0.5	1:0.5	8
Pt(50 nm)/Ti(5 nm)/SiO_2)		
P8-1.34	1:1.34	8
P4-0.5	1:0.5	4
P8-0.5	1:0.5	8

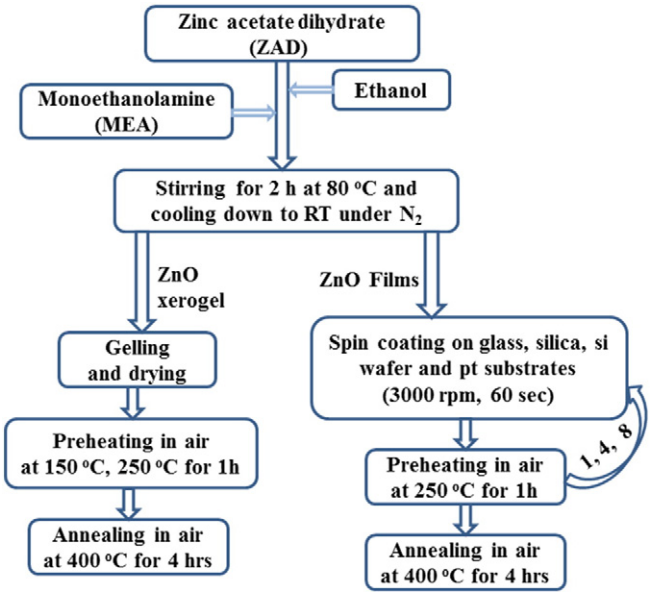

Fig. 1. Sol-gel preparation of ZnO xerogel powders and films.

ZnO sol was transferred into a glass syringe and filtered through Millipore Millex-FG Hydrophobic PTFE (Teflon) 0.2 μm before coating on oxygen plasma treated platinum substrates. Filtered ZnO sol was spin coated with 1300 rpm for 2 s (0 → 1300: 2 s), followed by 2000 rpm for 2 s (1300 → 2000: 2 s), and finally with 3000 rpm for 49 s (2000 → 3000: 1 s). Table 1 summarizes the multi-layer ZnO thin films obtained by coating ZnO sol of different composition on soda-lime glass, silica, silicon and platinum substrates.

After each layer deposition, films were kept for 20 min in air at room temperature and then preheated at 150 °C or 250 °C for different times. The resulting films were then annealed in air at 400 °C for 1 or 4 h, with the heating/cooling rate of 1 °C/min. The chosen annealing temperature (400 °C) was maintained by the thermal stability requirements of the Pt(50 nm)/Ti(5 nm)/SiO_2) substrate and was applied to the films deposited on all substrates. The final selected curing and annealing conditions are reported in Fig. 1.

2.3. Characterizations

The morphology of the films was observed by JSM-5500 scanning electron microscope (SEM) (JEOL technics Ltd.) with an accelerating voltage of 10 kV. The high magnification micrographs of the annealed films were obtained by field emission scanning electron microscopy (FE-SEM) operating at 5 kV with a Zeiss supra 60 scanning electron microscopy (BIOtech - University of Trento). SEM and FE-SEM images were acquired after the deposition of a thin gold layer by the SC7620 Mini Sputter Coater (VG Microtech). The thermal behavior of annealed ZnO xerogel powders has been investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a thermobalance STA 409 NETZSCH apparatus with a heating rate of 10 °C/min in air up to 500 °C. Fourier transform infrared spectroscopy (FT-IR) data was acquired in a transmission mode on a Thermo Optics Avatar 330 FTIR instrument in a 4000–400 cm^{-1} frequency range, using 64 scans and resolution of 4 cm^{-1}. The crystal structure of ZnO thin films and xerogel powders were analyzed by a Rigaku D-Max III X-ray powder diffractometer in glancing incidence configuration, using Cu-Kα radiation (λ = 0.154056 nm) and a graphite monochromator in the diffracted beam. In order to enhance the signal to noise ratio of ZnO films patterns, asymmetric scan geometry was adopted and measurements were performed in the 2θ range 30–40° with incident angle (θ) of 0.5°, sampling interval of 0.15° and 120 s as counting time. The selected 2θ range was adopted in order to eliminate the