Thin Solid Films 519 (2011) 6135–6139

Contents lists available at ScienceDirect

Thin Solid Films

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

Influence of annealing on humidity response of RF sputtered nanocrystalline $MgFe_2O_4$ thin films

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ARTICLE INFO

Article history:
Received 7 August 2010
Received in revised form 23 March 2011
Accepted 29 March 2011
Available online 6 April 2011

Keywords:
$MgFe_2O_4$ thin film
RF sputtering
Annealing temperature
Humidity sensing

ABSTRACT

Humidity response of Radio Frequency sputtered $MgFe_2O_4$ thin films onto alumina substrate, annealed at 400 °C, 600 °C and 800 °C has been investigated. Crystalline phase formation of thin films annealed at different temperature was analyzed by X-ray Diffraction. A particle/grain like microstructure in the grown thin films was observed by Scanning Electron Microscope and Atomic Force Microscope images. Film thickness for different samples was measured in the range 820–830 nm by stylus profiler. Log R (Ω) response measurement was taken for all thin films for 10–90% relative humidity (% RH) change at 25 °C. Resistance of the film increased from 5.9×10^{10} to 3×10^{12} at 10% RH with increase in annealing temperature from 400 °C to 800 °C. A three-order magnitude, 10^{12} Ω to 10^{9} Ω drop in resistance was observed for the change of 10 to 90% RH for 800 °C annealed thin film. A good linear humidity response, negligible humidity hysteresis and minimum response/recovery time of 4 s/6 s have been measured for 800 °C annealed thin film.

1. Introduction

Thin films of ceramic humidity sensor are gaining more interest due to growing demand of integrated sensors. Bulk and thick film of ceramic, carbon nano tube, inorganic, organic, polymeric based chemical sensor, gas sensor and humidity sensor have been extensively investigated. Although the inherent problems associated with these sensors are large response time, long-term drift, and less durability of sensor [1–5]. Humidity monitoring is an important parameter for most of characterization techniques, chemical processing, pharmaceuticals, and even superconducting phenomenon is also highly influenced by the humidity [6–10]. Therefore, significant efforts in developing materials and methods for fast and precise relative humidity (RH) sensing measurements are needed. Nanoparticles and bulk magnesium ferrite have been investigated for gas/humidity sensing application [11–13]. Among all ferrites, only a few reports are available on the fabrication of $MgFe_2O_4$ thin film [14–17]. The literature on magnesium ferrite thin films investigated for its magnetization studies is also reported scantly. No one has exploited magnesium ferrite thin film for humidity sensing despite bulk magnesium ferrite is a highly sensitive material for humidity sensing [18–20]. Most of the research and development work is being pursued for humidity response of TiO_2, Al_2O_3, ZrO_2, $BaTiO_3$, and polymers thin films [21–24]. Exploitation of magnesium ferrite thin film for humidity sensing would be highly beneficial for technological point of view.

In present work, we have prepared magnesium ferrite thin films by radio frequency (RF) sputtering and influence of post annealing temperature on humidity sensing properties has been investigated. The influence of microstructure on humidity sensing property has been analyzed. Decrease in electrical resistance was measured for 10–90% RH change at 25 °C for thin films. Response time and humidity hysteresis properties have been also discussed.

2. Humidity sensing mechanism

Humidity sensing by material is a surface adsorption phenomenon. The adsorption of water molecules on material surface takes place due to electrostatic field created by pores, defects and Lewis acid/base surface ions. Exchange of electron leads to the chemisorption process and it dissociates water vapors in H^+ and OH^- ions on such activated surface sites. There are three mechanisms proposed for explaining the experimentally proven increase of surface conductivity in the presence of water vapor. Two direct mechanisms were proposed by Heiland and Kohi [25] and the third, indirect, was suggested by Morrison [26] and Henrich and Cox [27]. The first mechanism of Heiland and Kohi attributes the role of electron donor to the "rooted" OH group. The water vapor interaction mechanism with metal oxide can be described as:

$$H_2O_{gas} + Mg^{\delta+} + O^{\delta-} \Leftrightarrow (Mg^{\delta+} - OH^-) + (OH^-) + e^- \quad (1)$$

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0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.03.120

where $Mg^{\delta+}$ and $O^{\delta-}$ are the magnesium ion (Lewis acid) and oxygen ion (Lewis base) on the surface react with water molecule to release an electron e^- for conduction. First chemisorbed OH^- layer is limited to monolayer. Due to high electrostatic field in the chemisorbed OH^- monolayer further more water molecules are adsorbed through hydrogen bonding on the hydroxyl groups of chemisorbed layer. It is known as first physisorbed water layer through H-bonding. Thus due to high electrostatic field H^+ ions hop from one water molecules to next neighboring molecule forming hydronium ion (H_3O^+) as indicated in following reactions [28]:

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \quad (2)$$

$$H_3O^+ \Leftrightarrow H_2O + H^+ \quad (3)$$

Hence, the proton starts conducting in a chain of physisorbed layer. As the protonic conduction begins, electrical resistance of sensor drops. In addition, at higher humidity the capillary condensation of water molecules in to open pores on surface is responsible for sensing capability of material, and is considered an important factor [29,30]. The schematic diagram of protonic conduction on material surface is shown in Fig. 1.

3. Experimental details

For the deposition of $MgFe_2O_4$ thin films by rf-sputtering, magnesium ferrite target was synthesized in our lab. Magnesium ferrite target was synthesized by conventional solid-state reaction method. MgO and Fe_2O_3 were taken in stoichiometric ratio1:1. Further, powder was ball milled for 30 h, the ratio of balls to material was taken 1:16. After ball milling, the powder mixture was kept in a ceramic crucible for calcinations at 1000 °C for 8 h in air in a muffle furnace. Calcined powder was again ground for 2 h in pastel mortar. Small amount of polyvinyl alcohol binder was added to make two-inch diameter $MgFe_2O_4$ target. It was followed by sintering at 1250 °C for 10 h. All necessary precautions were carried out to avoid cracks and bulging in target. Target thickness was maintained approximately 1 mm. Deposition of film was carried out on α-Al_2O_3 substrate by Ar^+ bombardment at a base pressure of 7 Pa for 2 h. Deposited films were annealed at 400 °C, 600 °C and 800 °C temperature for 2 h. Thickness measurements were done by "Stylus profiler". Thickness for sputtered film was obtained 820–830 nm for 2 h deposition. Gold electrodes were deposited by direct current, DC, magnetron sputtering through masking on the surface of thin film.

The humidity response measurements of the different samples were carried out by using a two pressure method based standard humidity generator (Thunder Scientific 2500 series). This generator creates humidity inside the $12'' \times 12'' \times 10''$ dimensional test chamber.

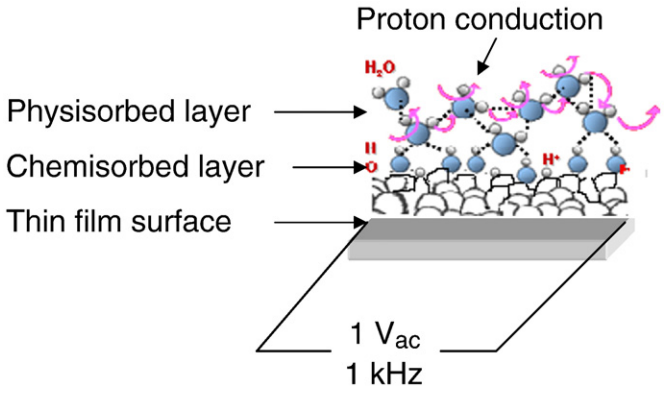

Fig. 1. Schematic diagram showing chemisorption and physisorption of water molecules on the $MgFe_2O_4$ thin film surface and protonic conduction.

The test chamber is made up of 300 stainless steel fluid jacket with proper isolation with environment. The uncertainty of RH generator is within $\pm 0.5\%$ RH. The resistance measurement was taken from 10 to 90% RH in steps of 10% RH at 25 °C. The two-pressure method humidity generator is based on the relation for relative humidity generation as:

$$\%RH = \frac{Pa}{Ps} \times 100 \quad (4)$$

where:

P_a = actual pressure of water vapor at fixed temperature
P_s = saturation pressure of water vapor at fixed temperature.

Humidity Generator operates on board multifunction central processing unit in conjunction with other peripheral cards to perform calculation and control functions.

Humidity response was taken at different frequencies 100 Hz, 1 kHz and 100 kHz, while best response was observed at 1 kHz. Thus all humidity responses were carried out at 1 kHz by Fluke 81 50 MHz Function Generator. One-volt alternating voltage was applied to avoid any polarization effect due to dipole moment of water molecules. High resistance of films was measured by Kiethley 6517A electrometer.

Phase determination was carried out by X-ray Diffractometer, XRD. Surface micro structure and energy dispersion spectroscopy, EDS, for elemental analysis studies were carried out by Scanning Electron Microscope, SEM. Atomic Force Microscopy, AFM, was used to observe average particle and pore diameter distribution of the films. For measuring conductance, gold electrodes were made by DC sputtering deposition technique.

4. Results and discussion

4.1. X-ray diffraction

XRD diffraction pattern of the films annealed at different temperatures was measured using Bruker AXS diffractometer as shown in Fig. 2. The diffraction pattern was measured at 40 mA, 40 kV condition with Cu Kα source and at 1° grazing angle. All the XRD peaks matched with spinel structure listed as per JCPDS card no.36-0398. Crystallite size was calculated, using Scherrer's formula; it increased from 22 nm to 48 nm with increasing annealing temperature

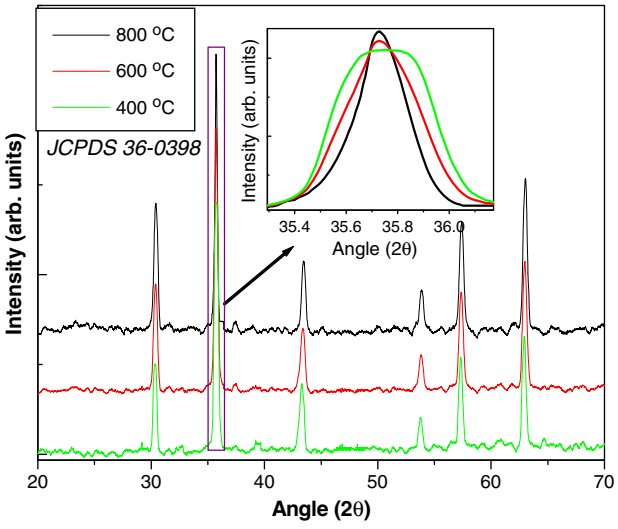

Fig. 2. XRD diffraction pattern for RF sputtered $MgFe_2O_4$ thin film annealed at 400 °C, 600 °C and 800 °C and zoom on peak (inset).