Thin Solid Films 520 (2012) 4523–4526

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Temperature behavior of electrical properties of high-k lead–magnesium–niobium titanate thin-films

Wenbin Chen [a,*], Kevin G. McCarthy [b], Mehmet Çopuroğlu [c], Shane O'Brien [c], Richard Winfield [c], Alan Mathewson [c]

[a] Electromechanical Engineering College, Guilin University of Electronic Technology, China
[b] Department of Electrical & Electronic Engineering, University College Cork, Ireland
[c] Tyndall National Institute, University College Cork, Ireland

ARTICLE INFO

Available online 21 December 2011

Keywords:
High-k
Thin-films
PMNT
Temperature

ABSTRACT

This paper reports on the temperature dependence of the electrical properties of high-k lead–magnesium–niobium titanate thin films processed with different compositions (with and without nanoparticles) and with different annealing temperatures (450 °C and 750 °C). These characterization results support the ongoing investigation of the material's electrical properties which are necessary before the dielectric can be used in silicon-based IC applications.

1. Introduction

Lead–magnesium–niobium titanate, $Pb(Mg_{0.33}Nb_{0.67})_{0.65}Ti_{0.35}O_3$ (PMNT) is a promising ferroelectric material due to its high dielectric constant and other material properties [1,2]. It is an attractive material for realizing high-performance and low-cost Metal–Insulator–Metal (MIM) capacitors. High performance MIM capacitors using PMNT have been proposed in previous work [3]. In this paper, the thin film characteristics under different test temperatures are measured, and an analysis of the resulting MIM capacitor measurements is presented.

2. Experimental details

2.1. Synthesis and film preparation and processing

All the chemicals employed were supplied by Sigma-Aldrich Co. Mg $(C_2H_5O)_2$, $Nb(C_2H_5O)_5$, $Ti(n\text{-}C_3H_7O)_4$, 2-methoxyethanol (2ME), formamide, and 1-hydroxy-cyclohexyl phenyl ketone (1HPK) were used as received. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ was dehydrated in a laboratory vacuum oven (Heraeus VT 5042 EK) at 70 °C for 16 h prior to use. A 0.5 M Pb $(Mg_{0.33}Nb_{0.67})_{0.65}Ti_{0.35}O_3 + 15\%$ PbO was synthesized by the sol–gel method, a flowchart of which is given in [4,5]. A clear yellow/light brown sol was obtained. 4% by volume of formamide (stabilizer) was added. The precise concentration was adjusted by adding extra 2 ME, where necessary [5].

PMNT thin films were grown on a $Pt(111)/TiO_2/SiO_2/Si$ substrate using a sol–gel technique. The sol–gel was spin-coated using a WS-400A-6NPP/LITE Spin-Coater (Laurell Technologies) at a spin rate of 3000 rpm for 30 s at room-temperature. The resultant films were annealed using a Jipelec Jetfirst 150 rapid thermal processor at two temperatures of 450 °C and 750 °C in O_2 atmosphere respectively [4,5]. The samples are distinguished by different anneal temperatures (450 °C or 750 °C) and by the presence or absence of nanoparticles (np). The composition of the nanoparticles used was the same as that of the material itself ($Pb(Mg_{0.33}Nb_{0.67})_{0.65}Ti_{0.35}O_3$). The average particle size of the nanoparticles is 50 nm. The film thicknesses are as follows: PMNT_450 (475 nm, estimated), PMNT_np_450 (475 nm, estimated), PMNT_750 (380 nm) and PMNT_np_750 (250 nm).

2.2. Characterization

The crystal structure of the thin films was investigated by X-ray powder diffractometer with the monochromatic Cu-K_α radiation (PANalyticalX'Pert PRO MPD). The XRD patterns were recorded in a 2Θ region from 10° to 60° using a 0.034° step and exposure time of 100 s/step. The strong signal belonging to the Pt substrate between 39.3° and 40.7° was manually removed. Removing these types of strong signals belonging to the substrates in XRD studies is a common practice because the intensity of remaining peaks are typically too low in comparison to that of the substrates [5]. This is done for presentation purposes only and does not influence the interpretation of the data. In order to quantify the intensity percentage of the perovskite phase, the following equation was used: % perovskite phase $= [I_{max}\,(\text{pero}) / (I_{max}\,(\text{pero}) + I_{max}\,(\text{pyro}))] \times 100$, where I_{max} (pero) and I_{max} (pyro) denote the intensities of the perovskite and pyrochlore phases, respectively [5].

Fig. 1 shows the XRD patterns for the PMNT samples annealed for a range of temperatures prepared by the standard chemical solution deposition method, and with added nanoparticles, respectively. It is

* Corresponding author. Tel.: +86 15907886352.
E-mail address: cwb0201@163.com (W. Chen).

0040-6090/$ – see front matter
doi:10.1016/j.tsf.2011.12.037

proposed that the presence of nanoparticle seeds of PMNT prevented the formation of the perovskite phase [4]. Scanning Electron Microscope (SEM) images of the 750 °C samples with and without nanoparticles have been shown in [4] and in these images the films all appear dense and compact with no evidence of porosity. The SEM images were obtained by an FEI NovaNano 630 model high-resolution SEM instrument whose operating voltage was 20 keV (the operating voltages were shown in their respective figures in [5]).

Following growth and annealing of the thin-films, a 100 nm Pt was deposited to form the top electrode for the PMNT thin film capacitors. 200 nm Au was subsequently deposited onto the top Pt layer to improve the electrical contact. The composite film was then patterned to form a series of square pad MIM capacitor test structures by photolithography.

3. Electrical properties

The measurements were performed using the square pad MIM capacitors on each sample. The edge-to-edge distance between the adjacent square pads is 25 μm, and the pads dimensions are 125 μm × 125 μm, giving a capacitor area of 15,625 μm^2 [6] (Fig. 2).

The capacitance as a function of voltage at 1 MHz was measured with a Hewlett Packard (HP) 4280A C–V meter. The capacitance was measured for each sample with the probes lifted in the air and also with the probes touching the metal patterns. The capacitance measured with the probes into the air was then subtracted from the measurements when the probes were contacted to the sample, to remove any offsets in the C–V measurement setup. The leakage current as a function of the applied voltage was measured using an Agilent B1500A Semiconductor Device Analyzer. All the measurements were performed on a Cascade Microchamber Attoguard probe station with a precision temperature controller. The emphasis of this research was to develop thin-film materials for high-performance capacitors in integrated circuits focusing on low voltage applications where the maximum applied voltage would not be more than a few Volts. The analysis of the C–V behavior of thin-films for IC applications is usually performed over a small voltage range e.g. −1.0 V to 1.0 V so as not to cause breakdown effects in the samples and this approach was used for the measurements presented here.

3.1. Capacitance–Voltage (C–V) measurements

Fig. 3 presents C–V measurements for the four different samples as outlined previously i.e. samples with an annealing temperature of either 450 °C or 750 °C and with or without nanoparticle seeds. In all cases, the bias voltage for C–V measurement has been swept from −1 V to 1 V and the capacitance has been measured at temperatures ranging from −50 °C to 75 °C.

For the PMNT_450 thin film (without nanoparticles) capacitor, the capacitance value increases as the temperature is increased from −50 °C to 75 °C. For the PMNT_np_450 thin film (with nanoparticles) capacitor, the capacitance value also increases as the temperature is

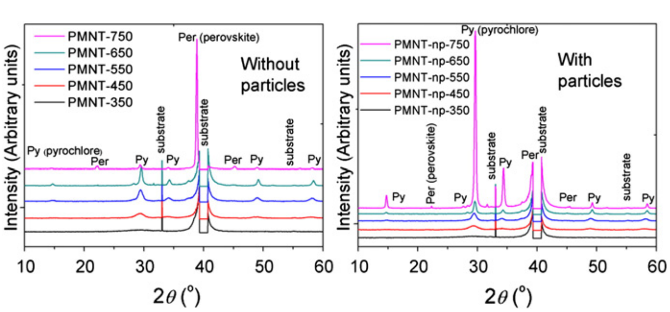

Fig. 1. XRD patterns of PMNT samples with and without embedded nanoparticles annealed at temperatures ranging from 350 °C to 750 °C.

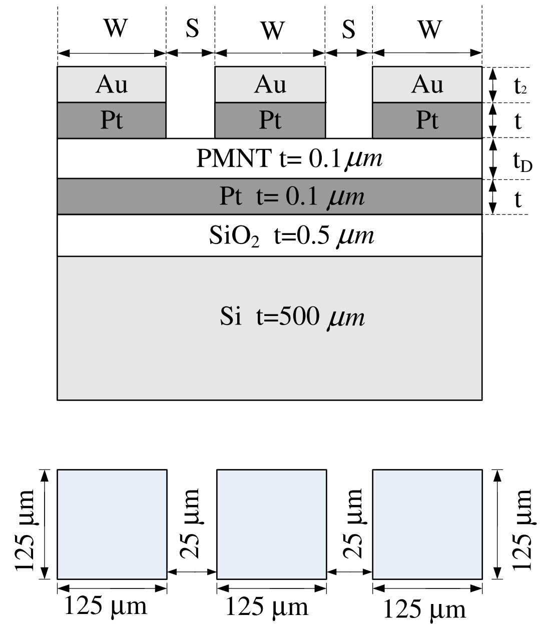

Fig. 2. Cross-section and top view of the PMNT square pad MIM capacitor test structures.

increased from −50 °C to 75 °C. Thus, both sets of samples annealed at 450 °C exhibit the same temperature behavior i.e. the capacitance increases with increasing temperature, whether nanoparticles are present or not. It is also noted that the capacitance obtained from the samples annealed at 450 °C are smaller in all cases than the capacitance obtained from the samples annealed at 750 °C.

The PMNT_750 thin film (without nanoparticles) also displays a capacitance that increases as the temperature is increased from −50 °C to 75 °C (at zero-bias) and it also shows a capacitance variation with applied bias. The capacitance behavior for the PMNT_np_750 thin film (with nanoparticles) is different to the other three samples. In this case, the capacitance value decreases as the temperature is increased from −50 °C to 75 °C, for bias voltages more negative than −0.25 V.

The samples annealed at 450 °C display constant capacitance for each test temperature, i.e. the capacitance is independent of DC bias. As the annealing temperature is increased to 750 °C, the capacitance values for the sample without nanoparticles are enhanced substantially which is a remarkable result. The samples annealed at 750 °C display an upward C–V trend, namely, a positive capacitance variation with DC bias [7]. This is typical dielectric behavior for amorphous oxide materials [7]. The variation of the capacitance with the applied voltage is the result of the use of thin multi-component oxide films of complex chemical composition. As presented in Fig. 3, high capacitance tunability is achieved while increasing further the annealing temperature, indicative of an improvement in the crystallinity.

When the capacitance for a certain structure is measured, the dielectric constant of the material can be found by rearranging the capacitance formula i.e.

$$C = \frac{\varepsilon_0 \varepsilon_r}{t_D} \cdot A \Rightarrow \varepsilon_r = \frac{C}{A} \cdot \frac{t_D}{\varepsilon_0} \quad (1)$$

Where ε_o is the permittivity of free-space, ε_r is the relative permittivity (dielectric constant) of the dielectric layer, t_D is the thickness of the dielectric layer and A is the area of the square pads. Based on the measured capacitance, the PMNT_450 sample exhibits an estimated ε_r value of 83, while the PMNT_np_450 sample exhibits an estimated ε_r value of 77. The PMNT_750 sample exhibits an ε_r value of 1050, while the PMNT_np_750 sample exhibits an ε_r value of 65. These values are