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Characterization of $ZrTiO_4$ thin films prepared by sol–gel method

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ABSTRACT

The electrical properties, memory switching behavior, and microstructures of $ZrTiO_4$ thin films prepared by sol–gel method at different annealing temperatures were investigated. All films exhibited $ZrTiO_4$ (111) and (101) orientations perpendicular to the substrate surface, and the grain size increased with increasing annealing temperature. A low leakage current density of 1.47×10^{-6} A/cm^2 was obtained for the prepared films. The *I–V* characteristics of $ZrTiO_4$ capacitors can be explained in terms of ohmic conduction in the low electric field region and Schottky emission in the high electric field region. An on/off ratio of 10^2 was measured in our glass/ITO/$ZrTiO_4$/Pt structure with an annealing temperature of 600 °C. Considering the primary memory switching behavior of $ZrTiO_4$, ReRAM based on $ZrTiO_4$ shows promise for future nonvolatile memory applications.

1. Introduction

With the development of digital electronics, memory has grained an important role in portable consumer electrical products, such as notebooks, digital cameras, video game consoles, USB flash devices and mobile phones. Recently, flash memory has become the mainstream nonvolatile memory devices; because, it has several drawbacks, including high operation voltage, low operation speed, and poor endurance. New nonvolatile memory devices, such as polymer random access memory, magnetic random access memory, phase change memory, and resistance random access memory, have been extensively investigated for future nonvolatile memory device applications. Among these new memory devices, resistance random access memory (ReRAM) shows excellent memory characteristics, such as a simple structure, excellent scalability, compatibility with the standard CMOS process, low-power operation, high-density integration, and high-speed write and erase operations [1,2]. For the ReRAM technology, it is widely believed that oxide materials, such as $SrZrO_3$, $PrCaMnO_3$, and binary oxide (ZrO_2, TiO_2, and Nb_2O_5) will be needed for resistors [2–6].

On the other hand, a ReRAM memory cell is a metal-insulator-metal (MIM) structure composed of insulating or semiconducting transition metal oxides that exhibit reversible resistive switching on applied voltage pulses [7]. In the resistive switching phenomenon, a large change in resistance (>1000%) occurs on applying pulsed voltages. A memory cell is in a highly resistive state and is put into a low-resistance state (LRS) by applying a high voltage stress in the so-called "forming process.". After the forming process, the device cell in a LRS is switched to a high-resistance state (HRS) by applying a threshold voltage; this is called the reset process [7]. Binary oxide semiconductors, such as ZnO, Sm_2O_3, HfO_2, CeO_2, GeO_2, Nb_2O_5, TiO_2, NiO, and ZrO_2, also show conductivity switching behaviors controlled by the external voltage or current [8–16]. $ZrTiO_4$ (ZrO_2–TiO_2) exhibits an orthorhombic crystal structure and possesses α-PbO_2-type structure belonging to the *Pbcn* space group [17]. $ZrTiO_4$ thin films have been further studied

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because of their excellent dielectric properties, such as the a dielectric constant and dielectric loss of 38 and 0.006, respectively [18,19]. However, $ZrTiO_4$ thin films fabricated by the sol–gel method have not been discussed in terms of ReRAM application. In this paper, we study the dependence of the microstructure, electrical properties, and memory switching behavior on the annealing temperature.

2. Experimental procedures

Film deposition was prepared using the sol–gel process, as shown in Fig. 1. High-purity zirconium isopropoxide ($C_{12}H_{28}O_4Zr$, 98% pure; Acros Organics) and titanium isopropoxide solution ($Ti \cdot C_{12}H_{28}O_4$, 70 wt% in 1-propanol, Fluka) were taken at a molar ratio of 1.0:1.0 and dissolved in 2-propanol [$(CH_3)_2CHOH$, 99.5%, J.T. Baker] solution at room temperature, and then the resultant solution was stirred at room temperature for 3 h. The concentration of the final solution was adjusted to about 0.2 M. The precursor sol was placed on the indium tin oxide (ITO)/glass substrate (Coring 7059 glass) and spun at 3000 rpm for 15 s and at 4000 rpm for 30 s to form precursor thin films. The coating processes were repeated five times. Finally, the films were annealed at various annealing temperatures ranging from 600 °C to 800 °C for 1 h (at a heating rate of 2 °C/min) in an air furnace for crystallization. The final thickness of the $ZrTiO_4$ films of five layers was about 750 nm, which was determined using scanning electron microscopy (SEM). The film

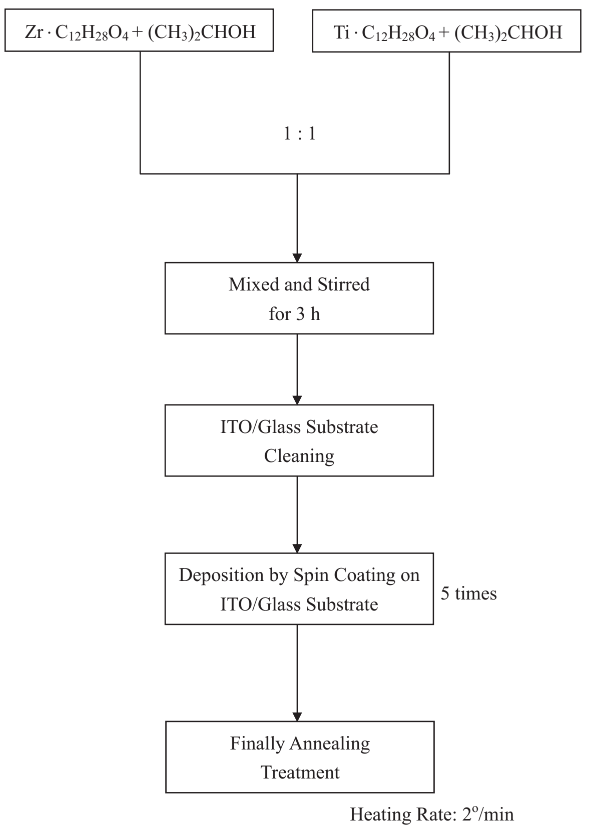

Fig. 1. Flow diagram of the $ZrTiO_4$ thin films using the sol–gel method.

structure was analyzed by X-ray diffraction (XRD, ATX-E, Rigaku) at 30 kV and 20 mA with Cu Kα radiation. The morphology of the film surface was determined with the use of an atomic force microscope (AFM, DI3000, Digital Instruments) with a silicon tip in tapping mode for each sample.

On the other hand, the leakage current characteristics and memory switching behavior of the $ZrTiO_4$ thin films were evaluated by current–voltage (*I–V*) measurements. The sample devices (glass/ITO/$ZrTiO_4$/Pt) were fabricated by symmetrically depositing Pt electrodes (1 mm diameter) on the top of the glass/ITO/$ZrTiO_4$ structure. All electrodes were prepared by using ion sputtering. The *I–V* curves of the metal/insulator/ITO structure were measured with the HP4155 Parameter Analyzer.

3. Results and discussion

Fig. 2 shows the XRD patterns of $ZrTiO_4$ thin films deposited on glass/ITO substrates at various annealing temperatures. The thin films were crystalline, which exhibits an orthorhombic crystal structure (JCPDS 34–0415) and possesses α-PbO_2-type structure belonging to the *Pbcn* space group as they were deposited at various annealing temperatures ranging from 600 °C to 800 °C for 1 h. The ITO peaks, such as $2\theta==22^\circ$ and 46°, appeared at various process parameters. As the annealing temperatures increased to 800°C, the intensities of the $ZrTiO_4$ peaks (1 1 1) were relatively increased, compared with the others, due to the higher orientation. To compare the X-ray diffraction patterns, the relative intensity ratio ($I_{111}/(I_{101}+I_{111}+I_{020}+I_{200}+I_{120}+I_{201}+I_{121}+I_{211}+I_{220}+I_{022}+I_{202}+I_{031}+I_{122}+I_{131})$) increased from 0.43 to 0.50 with the increasing annealing temperature. The kinetic energies and mobilities of the atoms also increase with increasing annealing temperature at the growing film. The additional energy contributed to finer and uniform grain development in the films. In addition, the full-width half-maximum (FWHM) intensity value of the XRD peak and the crystallite size are estimated in Table 1. The FWHM intensity values of the $ZrTiO_4$ increase from 0.35° to 0.54° as the annealing temperature decreases, which implies that a lower

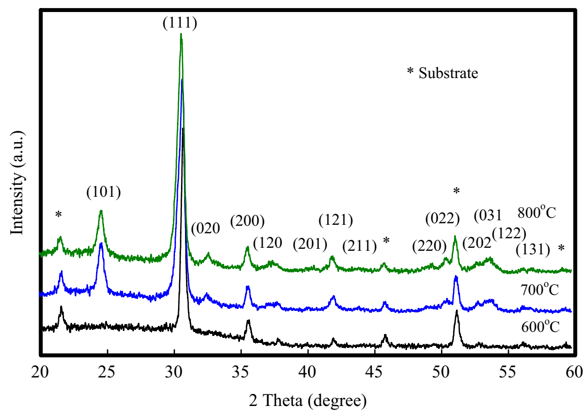

Fig. 2. X-ray diffraction patterns of the $ZrTiO_4$ thin films on various annealing temperatures.