Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Significantly enhanced energy density of amorphous alumina thin films via silicon and magnesium co-doping

Qian Feng, Manwen Yao*, Zhen Su, Xi Yao

Functional Materials Research Laboratory, School of Materials Science and Engineering, Tongji University, No. 4800 Caoan Road, Shanghai 201804, China

ARTICLE INFO

Keywords:
Amorphous Al_2O_3
Doping
Breakdown strength
Leakage current
Energy density

ABSTRACT

The different Si-Mg co-doping content was explored to improve the dielectric properties of amorphous Al_2O_3 thin film. According to the analysis of DSC, FT-IR, and XPS spectra, it can be confirmed that a novel structure of glass network is formed in the co-doped Al_2O_3 thin film. More importantly, compared to Al_2O_3 thin film, the leakage current of $(Al_{.97}Si_{.02}Mg_{.01})_2O_y$ thin film is reduced by 2 orders of magnitude and the breakdown strength is improved from 276 MV/m to 544 MV/m. The corresponding energy density of the modified sample is up to 9.2 J/cm^3, which is an enhancement of 6.2 J/cm^3 over that of the undoped Al_2O_3 thin film. Based on finite element analysis, the simulation results show that the applied electric field is mainly focused on the glass network, which could strengthen the stability of Al_2O_3 structure and decrease the breakdown probability of the films. From the viewpoint of defect chemistry, another reason for the enhancement of the dielectric properties is that Si-Mg co-doping results in the generation of cation vacancies and thus the formation of oxygen vacancies could be effectively prevented. This work could provide a new design strategy for high-performance dielectric capacitor devices.

1. Introduction

Advanced energy technologies in the 21st century create an urgent need for miniaturization, portability, large-scale integration, and low-cost energy storage components, such as electrostatic capacitors, which possess high power energy density and fast charge-discharge capability, as well as good environmental stability [1]. However, the best commercially available electrostatic capacitors only deliver a low energy density of ≈ 2 J/cm^3, which falls short of the ever-increasing demands for compact, reliable, and efficient electrical power systems [2]. Therefore, it is imperative to develop novel technologies that can significantly increase the energy density of the electrostatic capacitors [3]. Generally, the energy density (U_e) of dielectric capacitors is described by the integral:

$$U_e = \int EdD \tag{1}$$

and for linear dielectrics, U_e scales quadratically with E and linearly with ε_r as

$$U_e = 1/2\varepsilon_0\varepsilon_r E^2 \tag{2}$$

where ε_0 is the vacuum dielectric constant (8.8542×10^{-12} F/m), ε_r is the relative dielectric constant, and E is the electric breakdown strength [3–7]. The breakdown strength (E) that signifies the highest electric field applicable to the dielectric is the most critical parameter defining the energy density of the electrostatic capacitor. For this reason, polymers, such as biaxial-oriented polypropylene (BOPP), are the primary dielectric materials currently used in electrostatic capacitors due to their high E (> 700 MV/m), and low dielectric loss (< 0.02%). However, polymer dielectrics suffer drawbacks of low dielectric constants ($\varepsilon_r \approx 2$–3) and poor heat resistance. While inorganic materials, such as $BaTiO_3$ (BT), $Ba_xSr_{1-x}TiO_3$ (BST), and $PbZrTiO_3$ (PZT), possess large dielectric constants and excellent heat resistance [4–6,8–10]. Hence, inorganic dielectric materials with high dielectric constant and breakdown strength are preferred for the improvement of U_e of electrostatic capacitors.

Alumina (Al_2O_3) is a promising material for use in electrical and electric energy devices. Cost-efficient amorphous Al_2O_3 presents high breakdown strength (200–1000 MV/m), relative dielectric constant (7 − 10), band gap (≈ 9 eV), thermal stability (up to 1000 °C), and low leakage current [11–13]. In addition, Al_2O_3 thin films have been previously prepared using chemical vapor deposition (CVD), atomic layer deposition (ALD), molecular beam epitaxy (MBE), and magnetron sputtering techniques, which require high processing temperatures [11–13]. Compared with these approaches, sol-gel method is able to easily obtain the dense and homogeneous thin films, as well as accurately controls the chemical composition and phase structure at room

* Corresponding author.
E-mail address: yaomw@tongji.edu.cn (M. Yao).

https://doi.org/10.1016/j.ceramint.2018.03.135
Received 22 January 2018; Received in revised form 15 March 2018; Accepted 15 March 2018

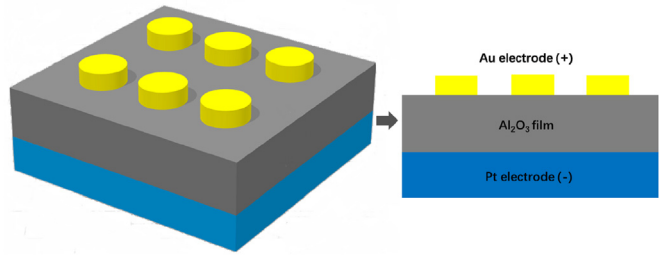

Fig. 1. Structure design of the samples.

temperature.

However, defects inside amorphous Al_2O_3 thin film are inevitable in the preparing process and lead to the decrease of the breakdown strength. Therefore, its further applications are limited. To address the issues, some elements, such as silicon [11], lanthanum [14], and titanium [15], were added into amorphous Al_2O_3 thin film to achieve substantial enhancement of E. Typically, silicon is a glass forming element capable of forming the glass network structure and improving the breakdown strength of the thin film. Magnesium incorporated into the glass network structure is beneficial for connecting the networks hence further gives rise to enhanced structural stability. Along this line, to produce a positive effect on the dielectric behavior, the novel amorphous Al_2O_3 thin film was designed and synthesized via co-doping silicon and magnesium. The experimental results indicate that the glass network is formed inside the Al_2O_3 thin films by co-doping Si and Mg. And the excellent dielectric properties of the co-doped films are achieved. Typically, a small co-doping of 2 mol% Si and 1 mol% Mg in Al_2O_3 matrix film concomitantly reduces leakage current by 2 orders of magnitude and raises breakdown strength up to 544 MV/m, which translates into a giant energy density of 9.2 J/cm^3, an enhancement of 202% over the undoped Al_2O_3 film (3.0 J/cm^3). And the dielectric properties agree well with the structure properties according to the investigation results. Besides, simulating the electric field distribution in the glass network region was carried out to explain the excellent dielectric properties. As a result of these favorable features, the simplicity and scalability of described approach provides a promising route to dielectric thin films materials for electrical energy storage applications.

2. Experimental

Al_2O_3 and $(Al_{1-0.02-x}Si_{.02}Mg_x)_2O_y$ (x = 0.5%, 1%, 2% and 5%) thin films (abbreviated as Al_2O_3, ASM0.5, ASM1, ASM2 and ASM5, respectively) were prepared by the sol-gel and spin coating technology. First, aluminum isopropoxide and 50 ml glycol ether were mixed together and stirred for 30 min at 60 °C. Next, tetraethyl orthosilicate and magnesium acetate were sequentially doped into the above solution. Then, 0.02 mol acetylacetone was added to control the rate of hydrolyze with stirring at 70 °C. After stirring for 30 min, the solution was catalyzed with 10 ml acetic acid at 80 °C. The mixture was stirred for another 30 min and then cooled down slowly to the room temperature to obtain the transparent and homogeneous sol.

The thin films were deposited by spin-coating process with a spin speed of 3000 rpm for 20 s for each layer on Pt/Ti/SiO_2/Si substrates. Before deposition, the substrates were ultrasonically cleared in acetone, deionized water and ethyl alcohol for 10 min, successively. After each coating layer, the films were preheated at 150, 300 and 450 °C for 5 min in sequence to form solid films by evaporating the solvents and burning the organic residues. After coating 7 layers, all of the samples were annealed at 450 °C for 3 h below their crystallization temperatures. The MIM (metal-insulator-metal) structure with Au top electrode in diameter of 1 mm was employed to measure the electrical properties (as shown in Fig. 1).

3. Results and discussion

3.1. Structural Analysis

Surface SEM images (Fig. 2) and cross-sectional SEM images (Fig. 3) show that the thin films annealed at 450 °C are of high quality and no crystallization or macroscopic imperfections (e.g. cracks and pores) presence. In other words, neither phase structure (remain amorphous) nor surface morphology (remain dense and uniform) is affected by Si-Mg co-doping. Cross-sectional SEM images (Fig. 3) also show that the

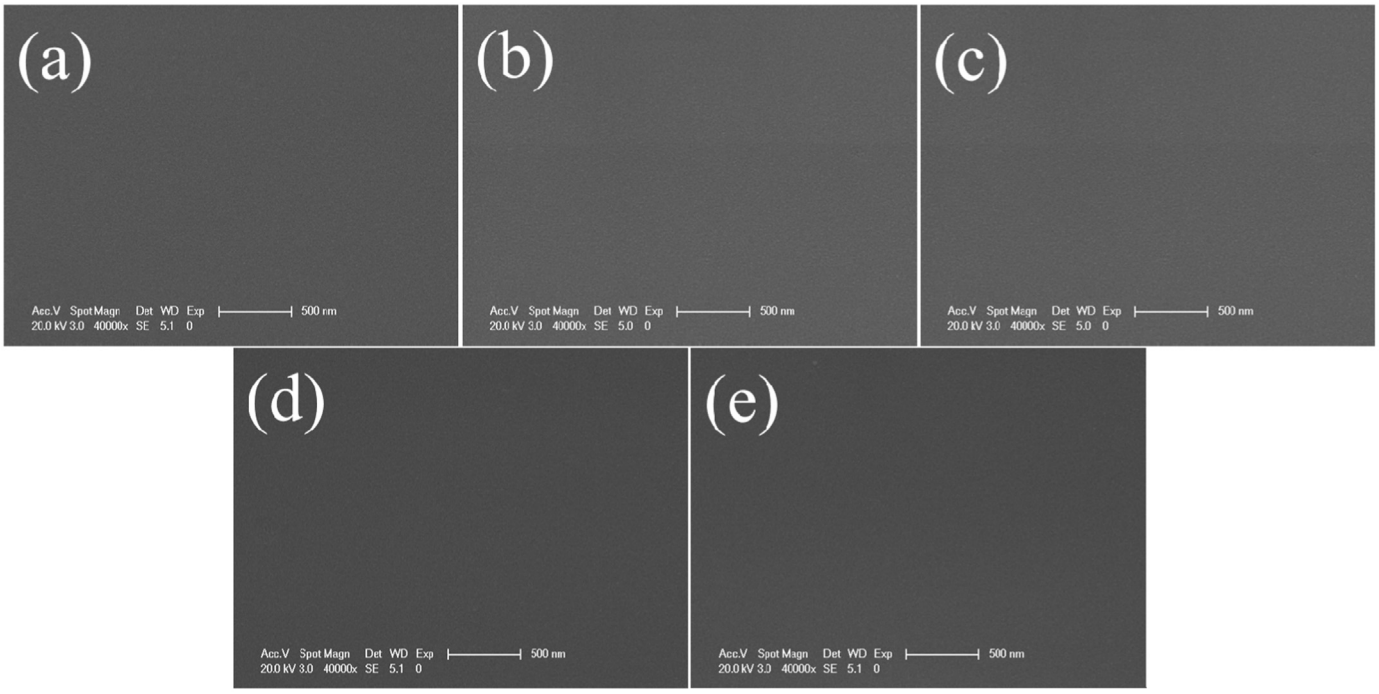

Fig. 2. Surface SEM images of the Al_2O_3 (a), ASM0.5 (b), ASM1 (c), ASM2 (d) and ASM5 (e) thin films.