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Leakage current and dielectric breakdown in lanthanum doped amorphous aluminum oxide films prepared by sol–gel

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Abstract

Dielectric $Al_{2-2x}La_{2x}O_3$ (x=0.00, 0.005, 0.02, 0.05, and 0.10) thin films were fabricated on Pt/Ti/SiO_2/Si substrates by sol–gel spin coating. The surface morphology of $Al_{2-2x}La_{2x}O_3$ thin film was observed by field emission scanning electron microscopy. The chemical state of the lanthanum in aluminum oxide films was analyzed using X-ray photoelectron spectroscopy (XPS), indicating that lanthanum reacts with absorbed water to form lanthanum hydroxide. *J–E* measurements were used to investigate the current conduction mechanism and breakdown behavior. The results show that La doping changes the conduction mechanism and makes influences on leakage current. The dominating conduction process of 10% La doped Al_2O_3 films turns into the space charge limited current (SCLC) mechanism in the field region ranging from 25 to 150 MV/m. The leakage current of the films with 10% La doping decreases by three orders of magnitude from 10^{-6} to 10^{-9} at the electric field of 25 MV/m. The breakdown strength increases with the increasing content of lanthanum.

Keywords: Aluminum oxide film; Leakage current; Lanthanum doping; Dielectric breakdown; MIM capacitors

1. Introduction

Dielectric thin films have attracted more attentions and been one of the predominant materials in semiconductor, capacitors and integrated circuits. Alumina thin film is usually known as promising dielectric materials owing to its extremely low leakage current density, large band gap (8.8 eV), relatively high dielectric constant (9–10), high breakdown field strength, thermal and chemical stability [1–4]. Furthermore, Al_2O_3, a promising candidate of so-called high relative permittivity, is a kind of highly insulating, optically transparent, and chemically stable dielectric material with many applications ranging from metallurgy to microelectronics [5,6]. The splendid electric properties make aluminum oxide films to be a candidate of dielectric material applied to energy storage capacitors. Energy storage density is proportional to the square of breakdown strength. Therefore, the enhancement in breakdown strength is beneficial to the improvement of energy storage density. The reliability of thin films stressed in high electric fields is a crucial issue for capacitors. For instance, the high leakage current can be destructive to the properties of devices.

The substitution influence of doping elements (La^{3+}, Mn^{3+}) on leakage current and ferroelectric properties has been studied in ferroelectric thin films and ceramics [7]. For example, the element of La^{3+}, Sm^{3+} replacing Bi^{3+} enhances the electrical properties in $BiFeO_3$ ceramics because of the decrease of Bi^{3+} volatilization and the number of oxygen vacancies [8].

The current conduction mechanism of ultrathin Al_2O_3 films as gate materials based metal–oxide–semiconductor (MOS) devices has been studied by many researchers [9]. The dominating current conduction of Al_2O_3 thin film involves Schottky emission (SE) [10] and Fowler–Nordheim (FN) tunneling [11]. However, there are very few reports on the leakage current and dielectric breakdown of La doped Al_2O_3

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thin films based on MIM (metal–insulator–metal) capacitors. Therefore, it is important to shed light on the effect of La on leakage current of aluminum oxide films by analyzing the possible conduction mechanism.

In this paper, we explored the chemical state of element and surface morphology of the $Al_{2-2x}La_{2x}O_3$ thin films. Additionally, an investigation has been performed on the effect of La doping on leakage current and breakdown behavior in aluminum oxide thin films.

2. Experiment

$Al_{2-2x}La_{2x}O_3$ ($x=0$, 0.005, 0.02, 0.05, and 0.1) thin films with titular represention as AL-0, AL-0.5, AL-2, AL-5, AL-10 were prepared by the sol–gel spin coating method. Aluminum isopropoxide ($Al(OC_3H_7)_3$) and Lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$) were used as Al-precursor and La-precursor, respectively. Firstly, both Aluminum isopropoxide and Lanthanum nitrate hexahydrate were dissolved in glycol ether with constant stirring for half an hour at 60 °C. Next, acetylacetone acting as chelating agent was added to restrain the hydrolysis of Aluminum isopropoxide. At the same time, the solution was continuously stirred for 30 min. A small amount of acetic acid as catalyst was added to the above solution. Subsequently, the obtained mixture was heated to 90 °C with agitation for 30 min. At last, the mixture was cooled down to room temperature to get a clear and homogeneous sol.

Thin films were deposited by spin-coating on layer-by-layer application (7 layers with a rotating speed of 3000 rpm for 20 s) on Pt/Ti/SiO_2/Si substrates. After each deposition, the films were preheated in a tubular furnace at 150, 300, 450 °C for 5 min, respectively to form solid films by evaporating the solvent and burning-out the organic residuals. Prior to spin coating, the substrates were rinsed in acetone, deionized water and ethyl alcohol using an ultrasonic bath for 10 min, respectively. The samples with 7 layers were annealed at 450 °C for 3 h with a heating speed of 3 °C/min and then cooled down to room temperature in a muffle furnace. The MIM structure with Au top electrode in diameter of 1 mm was employed to measure the electrical properties.

The undoped and La doped aluminum oxide thin films were characterized for surface morphological properties by field emission scanning electron microscopy (FESEM) (S-4700, HITACHI, Japan). The film thickness was measured by the cross-sectional FESEM images. The chemical state of lanthanum in La-doped Al_2O_3 thin films was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi). Measurements of electrical properties were performed by leakage current and dielectric breakdown strength. The current as a function of voltage was measured by using a Keithley 2400 source meter unit interfaced with a computer to perform the measurement and record data. Voltage was applied to a certain value in a successive voltage step of 0.2 V with delay time of 0.1 s, until the leakage current increased sharply and abruptly, indicating the occurrence of breakdown. The positive voltage was applied on top Au electrode acting as anode, while Pt was used as bottom electrode. In the experiment, 10 breakdown trials were measured for each sample to estimate the breakdown strength through Weibull distribution function due to the randomness of the dielectric breakdown.

3. Results and discussion

The surface morphology of aluminum oxide thin films with 0, 0.5, 2, 5 and 10 mol% La is shown in Fig. 1. There is no obvious change in the surface morphology with the increasing of La concentration. The film surfaces are seen to be smooth and uniform which shows no crystallization for undoped and La doped aluminum oxide films when annealed at 450 °C. According to the above results, both phase structure (remain amorphous) and surface morphology are not influenced by La doping. The thickness values of thin films measured by cross-sectional SEM images are 232, 205, 227, 232, 196 nm for AL-0, AL-0.5, AL-2, AL-5, AL-10, respectively.

XPS analyses on the AL-10 thin film surface were performed aiming to explore the chemical bonding of La^{3+} to determine the existence form of lanthanum in thin films. The binding energy has been calibrated by locating the C1s at 284.60 eV. The survey XPS spectrum of AL-10 shown in Fig. 2 suggests that there are no other metal elements on the surface except for Al and La. The binding energy of $La3d_{3/2}$ and $La3d_{5/2}$ is 851.8 and 835.4 eV, respectively. Moreover, Fig. 3 further displays the XPS spectrum of $La3d_{5/2}$. The $La3d_{5/2}$ spectrum splits into two sub-peaks, and the binding energy separation between main and satellite peak $\Delta E=3.70$ eV and intensity ratio of each multiple-split component are in good agreement with compound of $La(OH)_3$ ($\Delta E=3.7$ eV) [12]. In Fig. 4, it can be seen that O1s has two peak positions, indicating two oxygen species present on the surface. The peak at binding energy of 531.0 eV relates to metal oxides [13] while the peak at higher binding energy of 532.2 eV is attributed to lanthanum hydroxides [14]. Based on above results, it can be concluded that the element lanthanum exists in the form of $La(OH)_3$ in the film.

As reported in other articles, in the high field region, different conduction mechanisms being bound up with the leakage current in dielectric films have been discussed such as Schottky mechanism, Poole–Frenkel emission, and space charge limited current (SCLC) [15]. In the case of Schottky effect, carries are emitted from electrode surface to conduction band of the semiconductor. The current density dependence of electric field is given by [16]:

$$J = A * T^2 \exp\left[\frac{\beta_s E^{1/2} - \phi_S}{K_B T}\right] \quad (1)$$

$$\beta_S = \left(e^3/4\pi\varepsilon_r\varepsilon_0\right)^{1/2} \quad (2)$$

where A^*, ϕ_s, K_B, E, ε_r, ε_0 and T denote the barrier height, the Boltzmann constant, the electric field, the high frequency dielectric constant, the permittivity of the free space and the temperature (in Kelvin), respectively.

Poole–Frenkel emission is known as the bulk limited conduction mechanism which is generated due to the field strengthened