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Facile synthesis of AlO_x dielectrics via mist-CVD based on aqueous solutions

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ABSTRACT

Aluminum oxide (AlO_x) thin films were synthesized by mist-chemical vapor deposition (mist-CVD) using aluminum acetylacetonate ($Al(acac)_3$) dissolved in an aqueous solvent mixture of acetone and water. Nitrogen gas was used to purge the precursor solution and growth rates between 7.5–13.3 nm/min were achieved at substrate temperatures of 250–350 °C. The AlO_x layers deposited at temperatures below 350 °C exhibit 3–5 at% residual carbon levels, however those grown at 350 °C exhibit only 1–2 at% carbon impurity. Reasonable dielectric properties were obtained in the latter, with a dielectric constant (κ) of ~ 7.0, breakdown field of ~ 9 MV/cm and relatively low leakage current density of ~ 8.3×10^{-10} A/cm^2.

1. Introduction

Aluminum oxide (AlO_x) is a typical high-k material with high dielectric constant (~9.34), excellent thermal stability and wide band gap energy of 7.7–9.0 eV [1–3]. Such excellent properties make aluminum oxide a suitable material for use in electronic devices, for example as the gate insulator in thin film transistors or as passivation layers in organic light emitting diodes (OLED) and solar cells [4,5]. Several techniques are reported for the synthesis of AlO_x layers, including sputtering [6], metal organic chemical vapor deposition (MOCVD) [7], atomic layer deposition (ALD) [8], spray [9,10], and sol-gel techniques [11]. Among those, the ALD method has been extensively employed to deposit high quality AlO_x films, despite the relatively slow growth rate (< 1 nm/cycle) and the use of explosive precursors such as tri-methyl aluminum (TMA) [12]. Solution processes have also been studied for the synthesis of dielectric layers, however due to most of them necessitate the use of rather toxic solvents and high temperature post-deposition annealing. In order to overcome such disadvantages, recent efforts in the development of eco-friendly (non-toxic), low-cost processes for the synthesis of dielectric materials have been made by several research groups. For example, ink-jet printing, and sol-gel methods have been demonstrated using water, ethanol, acetone (aqueous solvents) and stable precursors such as aluminum acetylacetonate ($Al(acac)_3$), $AlCl_3$, $Al(NO_3)_3$ in air, although certain levels of impurity may be present in the resulting films [13,14].

An alternative scheme involves the Mist-CVD process, in which thin films are deposited by the thermal decomposition of a precursor mixed in various solvents, resulting in relatively simple and fast growth under atmospheric pressure without the need for expensive vacuum systems. Reports on Mist-CVD are available in the literature, on the production of metal, metal oxide, and other metal alloys. Kawaharamura et al. deposited AlO_x films using $Al(acac)_3$, methanol and water, at temperatures between 300 and 450 °C [15]. Jeon et al. also produced ZnO layers using a solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.15 M) over a substrate temperature range of 200–300 °C [16]. In another study conducted by Okuno et al. SnO_2 thin films were grown using $SnCl_2$, di-water (0.05 M) mixed with HCl at temperatures between 400 and 800 °C [17]. In addition, functional oxide thin films such as In_2O_3 and SnO_2 have been very recently reported in various solvents [18–20].

In the present work, a simple and environment friendly Mist-CVD method is demonstrated for the growth of AlO_x dielectrics. Aqueous solutions of $Al(acac)_3$ dissolved in a mixture of acetone and deionized (DI) water are used, at substrate temperatures between 250 and 350 °C. The growth behavior, surface morphology, chemical composition and dielectric properties of the Mist-CVD AlO_x layers are examined. The highest deposition temperature results in pinhole free AlO_x with high dielectric constant (~ 7.0), reasonable dielectric breakdown field (~ 9 MV/cm) and low leakage current density (~

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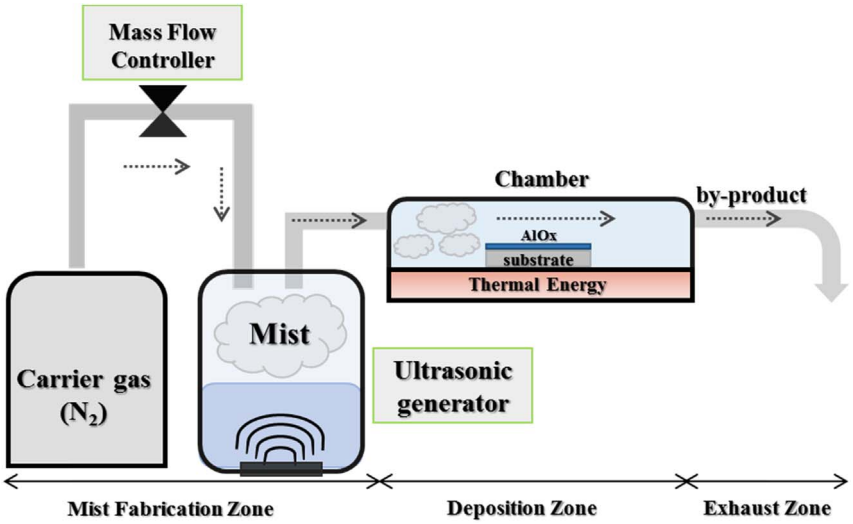

Fig. 1. A simple schematic illustrating the mist-CVD process.

8.2×10^{-10} A/cm^2).

2. Experimental

2.1. Precursor solution preparation

The liquid precursor solution for Mist-CVD was prepared by dissolving aluminum acetylacetonate (0.04 M, Aldrich) in a mixture of acetone (CH_3COCH_3) and deionized (DI) water (H_2O). The acetone to DI-Water ratio was 9:1. Here, the DI water reacts with the metal precursor to produce an AlO_x precursor solution. The solutions were stirred at 60 °C in air for 90 min.

2.2. AlO_x film deposition and device fabrication

The growth of AlO_x layers was carried onto p^{++} doped Si substrates by Mist-CVD using the above aluminum solutions, at substrate temperature between 250 and 350 °C. The native oxides were removed by RCA cleaning prior to the film growth. Fig. 1 consists of a simple schematic illustrating the Mist-CVD process steps. The aluminum solution was mystified an ultrasonic generator (f =1.6 MHz). The mist was next introduced into the reaction chamber with nitrogen (N_2) carrier gas, at a flow rate of 4 standard liter per minute (SLM). The subsequent AlO_x growth on the substrates was performed in the chamber under ambient atmosphere. Disk-shaped ITO (Indium Tin Oxide) electrode contacts (thickness ~100 nm) were used to measure the capacitance, leakage current and breakdown field of the AlO_x dielectrics.

2.3. Film characterization

NMR ^{1}H (Ascend™ 400, Scientific) studies were done to investigate the complex formation of Al(acac)$_3$ complexes in aqueous solution. The properties of the precursor solution were examined using thermal gravimetric analyses and differential scanning calorimetry (TGA -DSC, STA PT1600Thermostar). To estimate the thickness and refractive index values of the AlO_x films, spectroscopic ellipsometry (SE, Elli-SE(UV)-FM8) was performed. The microstructure of the layers was studied by X-ray diffraction (XRD, Rigaku diffractometer) with Cu Kα radiation (λ=1.5418 Å). The surface morphology and root mean square (RMS) roughness of the AlO_x films were obtained by atomic force microscopy (AFM, XE-100). X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific) depth profiles were obtained in order to verify the presence of residual carbon contaminant. The current-voltage (I-V), capacitance-voltage (C-V), and capacitance-frequency (C-F) analyses were performed using an HP- 4284A semiconductor parameter analyzer, to measure the breakdown field, leakage current, and dielectric constant, respectively.

3. Results and discussion

The precursor solution was examined to confirm the presence of Al(acac)$_3$ molecules, by NMR ^{1}H analyses. A Bruker Ascend 400 MHz NMR instrument was used, with $CDCl_3$ (deuterated chloroform) as the solvent. Fig. 2(a) consists of a spectrum that was collected from Al(acac)$_3$ powder dissolved in $CDCl_3$, which indicates the presence of methyl group resonance from Al(acac)$_3$ molecules at δ=2.00 ppm, and the β-CH resonance at δ=5.48 ppm [21]. Fig. 2(b) is the spectrum recorded from the AlOx precursor solution dissolved in $CDCl_3$, which shows the resonance information from the Al(acac)$_3$ molecules δ=1.98 ppm. The NMR analyses therefore indicate that the Al(acac)$_3$ molecules are well preserved in the AlO_x precursor solution, and that their decomposition shall only occur in the deposition chamber during the film growth process.

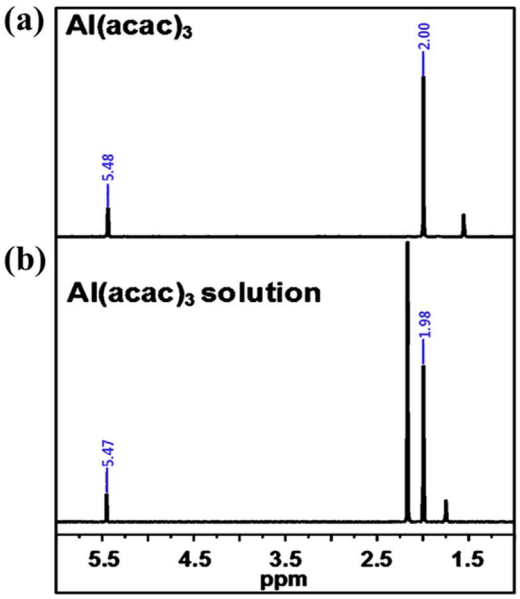

Fig. 2. ^{1}H NMR spectra of (a) Al(acac)$_3$ precursor and (b) Al(acac)$_3$ solution dissolved in a mixture of DI water and acetone with 9:1 ratio.