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Atomic layer deposition and characterization of stoichiometric erbium oxide thin dielectrics on Si(1 0 0) using $(CpMe)_3Er$ precursor and ozone

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ABSTRACT

Thin stoichiometric erbium oxide films were atomic layer deposited on p-type Si(1 0 0) substrates using tris(methylcyclopentadienyl)erbium and ozone. The film growth rate was found to be 0.12 ± 0.01 nm/cycle with an atomic layer deposition temperature window of 170–330 °C. X-ray photoelectron spectral (XPS) analysis of the resulting Er_2O_3 films indicated the as-deposited films to be stoichiometric with no evidence of carbon contamination. Studies of post deposition annealing effects on resulting films structures, interfaces, surface morphologies, and electrical properties were done using Fourier transform infrared spectroscopy, XPS, glancing incidence X-ray diffraction, optical surface profilometry, and *C–V*/*I–V* measurements. As-deposited Er_2O_3 films were found to start crystallizing in the cubic structure with dominant (2 2 2) orientation; no erbium silicate was found at the interface. After annealing at 800 °C in N_2, a new XPS feature was found and it was assigned to the formation of erbium silicate. As the annealing temperature was increased, the interfacial erbium silicate content was found to increase in the temperature range studied. Electrical characterization of Er_2O_3 thin gate dielectrics annealed at 600 °C exhibited higher dielectric constant ($\kappa = 11.8$) than that of as-deposited films (9.8), and a remarkably low hysteresis voltage of less than 50 mV along with a leakage current density of 10^{-7} A cm^{-2} at 1 MV cm^{-1}.

1. Introduction

Structural, interfacial, and electrical studies of high dielectric constant (κ) materials are important in the continuous scaling of nanoelectronics such as complementary metal oxide semiconductors (CMOS) and dynamic random-access memories (DRAM) [1]. The use of traditional SiO_2 as a gate dielectric layer less than 1.5 nm-thick has reached its fundamental limit because of the excess direct tunneling leakage current. So far, various lanthanide oxides, such as Gd_2O_3, Pr_2O_3, and Er_2O_3, have been considered as possible alternative gate dielectrics [2–8]. From these oxides, Er_2O_3 attracts increasing attention in terms of its large conduction band offset to Si (3.5 eV), moderately high dielectric constant (i.e. 9–14) and good thermal stability with silicon [2,9–11]. In addition, when compared with other lanthanide elements, erbium has appropriate electronegativity and small ionic radius, which result in limited tendency to hydroxylation [12].

Er_2O_3 has been grown with various deposition techniques, such as RF sputtering [13], electron beam evaporation [14], metal–organic chemical vapor deposition (MOCVD) [15,16], and atomic layer deposition (ALD) [7,17,18]. Among these techniques, ALD has been identified as a preferred technique for high-κ applications in order to maintain precise thickness at the needed dimensions within metal oxide semiconductor field effect transistors and to provide conformal coverage along the deep trenches of DRAM cells [1]. In early ALD studies of Er_2O_3, the precursor used was mainly tris(2,2,6,6-tetramethyl-3,5-heptanedione) erbium, $Er(thd)_3$. For example, Paivasaari et al. used $Er(thd)_3$ with ozone as the oxidant and found the deposition process has a low growth rate (~0.025 nm/cycle) at temperatures between 250 and 375 °C [17]. The resulting erbium oxide thin films were reported to be oxygen-rich (O/Er = 1.7) with carbon, hydrogen and fluorine contents of 1.8, 4 and 1.7%, respectively. A higher growth rate and reduced impurities were demonstrated by using tris(amidinate) precursors, $Er(tBu_2amd)_3$, and ozone [7], i.e. ~0.05 nm/cycle at 270 °C. However, the growth rate was reported to increase with precursor pulse duration, which was likely due to partial thermal decomposition of $Er(tBu_2amd)_3$ during the precursor delivery process; the stoichiometric ratio O/Er of those films was found to be 1.8 with a carbon content of 1.8%. In both studies of β-diketonate and amidinate types of erbium precursors, as-deposited Er_2O_3 was found to be amorphous at deposition temperatures below 250 °C, but started to crystalize into polycrystalline cubic

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structure at a temperature of 250–350 °C. Recently, cyclopentadienyl precursors were used to deposit other metal oxide films [19–21]. When compared with β-diketonate and amidinate ligands precursors, cyclopentadienyl-type precursors exhibit good thermodynamic stability. In addition, cyclopentadienyl compounds have a relatively low sublimation temperature which leads to a high ALD growth rate due to its moderate vapor pressure [6,22]. Tris(methylcyclopentadienyl)erbium, $(CpMe)_3Er$, was used with water vapor to deposit Er_2O_3 thin films on silicon [18]. The deposition rate was reported to be ~0.15 nm/cycle at 250–350 °C; the resulting films were found to be overstoichiometric (O/Er = 1.7) with a carbon content of ~2.5%. The oxygen-rich O/Er composition was attributed to hydroxylation reaction between erbium oxide and water vapor.

In this study, the cyclopentadienyl ligand erbium precursor tris(methylcyclopentadienyl)erbium is used with ozone as the oxidant to deposit Er_2O_3 thin films on silicon(1 0 0) by ALD. A wide ALD window as well as a growth rate of 0.12 nm/cycle is found. Elemental quantitative analysis of as-deposited Er_2O_3 films indicates that the films are *stoichiometric* (O/Er = 1.5) with *no* evidence of detectable carbon contamination. Post deposition annealing temperatures of 600–1000 °C are used for studies on the annealing behavior of the resulting ALD films; after annealing, changes in Er_2O_3 film structure, interfacial layer, and surface morphology are presented and discussed using a variety of analytical techniques. Further, electrical measurements of Er_2O_3 gate dielectrics on p-type Si before and after post deposition annealing are carried out and the effect of annealing on the electrical properties of the dielectric is investigated.

2. Experimental

Erbium oxide thin films were deposited using tris(methylcyclopentadienyl)erbium precursor and ozone as oxidant on Si(1 0 0) substrates in a horizontal hot wall tubular ALD reactor using a quartz tube 38 mm in diameter and 48 cm in length (Fig. 1). The reactor can be operated at a temperature up to 600 °C (custom-modified processing furnace, model 1043 Marshall, ThermCraft, Inc.) and typical depositions can be carried out at the temperature range of 25–450 °C. The base pressure of the ALD reactor was less than 20 mTorr. The oxidant was mixture of ozone and oxygen (1000 ppm ozone) generated with an oxygen (99.999% purity) flow through a UV lamp ozone generator immediately upstream of the deposition reactor. Argon (99.999% purity) was used as both carrier gas for the metal precursor and purging gas to clean the system between the delivery of precursor and oxidant. The precursor bubbler was kept at 95 °C, and the delivery line section from the bubbler to the reactor was maintained 20–30 °C higher than the bubbler temperature in order to prevent condensation of the precursor during delivery. The depositions of Er_2O_3 films were carried out at a total pressure of 500 mTorr and in the temperature range of 100–400 °C.

Er_2O_3 films were deposited on p-type Si(1 0 0) substrates (15 mm × 20 mm). Prior to deposition, substrates were cleaned with a 1:1:5 NH_4OH:H_2O_2:H_2O solution for 15 min to remove organic contaminants and particles, followed by 1% HF dip for 10 s. Each of the steps was followed by thorough deionized (DI) water rinse and drying by N_2 gas. This cleaning was found to leave ~0.5 nm (as measured by ellipsometry) of native oxide on the silicon substrate surface.

Thicknesses of as-deposited films were measured with a spectral ellipsometer (J.A. Woollam Co., Inc., model M44). Post deposition annealings were carried out in a preheated quartz horizontal furnace (Lindberg Blue three-zone furnace) under N_2 atmosphere for 5 min between 600 and 1000 °C at 1 atm. Fourier transform infrared (FTIR) spectroscopy (Nicolet, Magna-IR 560) was used in the transmission mode over the wavelength range of 4000–400 cm^{-1}. A high resolution X-ray diffractometer (Philips X'pert) configured with 0.1542 nm X-ray emission line of Cu with bandwidth of 0.05 nm as the excitation source was used to obtain glancing incidence X-ray diffraction (GIXRD) diffractograms of ~30 nm-thick as-deposited and post annealed Er_2O_3 films at 600, 800 and 1000 °C in N_2 (99.999% purity) at 1 atm. GIXRD diffractograms were collected at an incident angle of 0.7° to enhance the diffraction sensitivity within the film and to avoid interference from the single crystal Si(1 0 0) substrate. The peaks were identified using the International Centre for Diffraction Data (ICDD) database of diffraction pattern Powder Diffraction Files (PDF). Chemical bonding and elemental analyses of Er_2O_3 films were probed with high resolution X-ray Photoelectron Spectroscopy (XPS) (Kratos Analytical Ltd., Kratos AXIS-165) equipped with a monochromatic Al Kα (1486.6 eV) X-ray source operating at 15 kV and 10 mA. High resolution spectra were collected at a take-off angle 90° with pass energy of 20 eV, step size of 0.1 eV, and dwell time of 200 ms. Surface

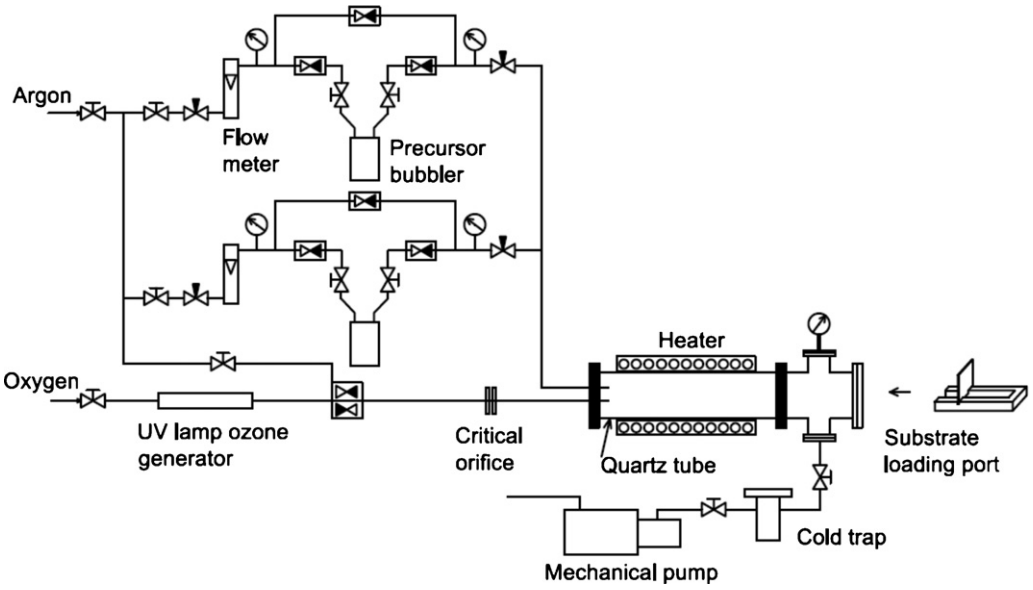

Fig. 1. Schematic diagram of the ALD system used for the deposition of erbium oxide films on Si substrates from tris(methylcyclopentadienyl)erbium and ozone.