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Influence of process parameters on atomic layer deposition of ZrO_2 thin films from $CpZr(NMe_2)_3$ and H_2O

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ABSTRACT

Atomic layer deposition of ZrO_2 films from tris(dimethylamino)cyclopentadienylzirconium $CpZr(NMe_2)_3$ and H_2O, was investigated using real-time characterization of the growth process and post-growth measurements of the films. Self-limited nature of the deposition process was observed at substrate temperatures ranging from 120 to 350 °C. In this temperature range growth rate of 0.08–0.1 nm per cycle was obtained on silicon substrates. The films deposited on silicon substrates at 200 °C and higher temperatures contained tetragonal and monoclinic phases of ZrO_2. The phase composition of the films depended on the deposition temperature as well as on the film thickness. The concentration of carbon residues decreased with increasing deposition temperature and did not exceed 0.9 at.% in the films deposited at 250 °C and higher temperatures. The refractive indices and densities of films grown from $CpZr(NMe_2)_3$ and H_2O at 250–350 °C ranged from 2.15 to 2.20 (at a wavelength of 633 nm) and 5.6 to 6.0 g/cm^3, respectively, being close to the highest values obtained for films deposited from $ZrCl_4$ and H_2O. The former process ensured, however, more uniform nucleation of ZrO_2 on graphene than the latter process did.

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1. Introduction

Zirconium dioxide (ZrO_2) is a dielectric with relatively wide band gap, high refractive index and high dielectric constant. These properties make ZrO_2 very attractive for application in optical [1] and electronic [2–6] devices. For instance, significant efforts have been focussed on characterization of ZrO_2 thin films prepared by various deposition techniques for silicon-based metal-oxide-semiconductor devices [3,4] and capacitor structures with TiN electrodes [5,6]. In addition, inspired by the many potential applications, deposition of ZrO_2 onto graphene [7–9] has been studied.

Among the deposition methods, which can be used for these purposes, atomic layer deposition (ALD) is the one that allows precise and simple thickness control and uniform coating of surfaces with complex shapes. One of the earliest and most commonly studied methods for ALD of ZrO_2 is the $ZrCl_4$–H_2O process, which has several disadvantages like rather high evaporation temperature of the precursor [10–12], chlorine contamination of the films [11,12] and generation of corrosive HCl as a reaction by-product. For these reasons, it is important to find and/or develop alternative fabrication methods and/or precursor combinations. In particular, reduction of the concentration of electrically active impurities to very low values is of marked significance in electronic applications that require low leakage current densities of ZrO_2 dielectrics and/or preventing unintentional trapping of electrons.

In earlier studies, Niinistö et al. [13] have demonstrated self-limiting nature of a process based on $CpZr(NMe_2)_3$ ($Cp = C_5H_5$; $Me = CH_3$) and ozone. In a relatively wide range of growth temperatures (T_G), high growth rate, conformity and low impurity concentrations of the resulting films have obtained. Although alkylamido-cyclopentadienyl-type precursors have problems with thermal stability at higher deposition temperatures, the reaction by-products should not be that corrosive and therefore $CpZr(NMe_2)_3$, known also as Zy(ALD), has already found application in electronic industry.

At the same time not only the selection of the metal precursor but also the choice of the oxygen precursor is important due to its influence on the growth rate, temperature range of ALD-type growth and/or film properties [14]. In some cases, application of H_2O instead of ozone is of particular significance due to the detrimental influence of ozone on the substrate material. For instance, deposition of thin films on graphene in ozone-based processes has led to significant degradation of graphene [15]. Moreover, application of ozone sets some additional requirements to the design of ALD reactors.

To expand the application range of $CpZr(NMe_2)_3$ we studied the possibility to use water vapor as an alternative oxygen precursor in

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combination with this metal precursor. We investigated growth rate, growth mechanism, nucleation, structural characteristics and density of thin films. Significant attention was focussed also on the surface roughness and refractive index of the films, because the latter parameters are important in optical coatings that also belong to the main application areas of ZrO_2 [1,16,17]. The characteristics of the films were compared with those of the films deposited from $ZrCl_4$ and H_2O in the same reactor. The research was focussed on films deposited on silicon substrates but, in a few experiments, we explored possibilities to apply these precursor combinations for ALD of ZrO_2 also on graphene as a prospective material for electronic devices of new generations.

2. Experimental details

2.1. Film growth

The ZrO_2 films studied in this work were deposited in an in-house built flow-type ALD reactor [18]. The ALD cycle used contained Zr precursor pulse, purge of the reaction zone with carrier gas, H_2O pulse and the second purge. Nitrogen (N_2 of 99.999% purity, Eesti AGA AS) was used as the carrier and purge gas. The pressure of nitrogen was kept at 200–220 Pa in the reaction zone during the deposition. The films were deposited from $CpZr(NMe_2)_3$ (Air Liquide) and H_2O at T_G of 70–400 °C and from $ZrCl_4$ and H_2O at 180–600 °C [11]. For characterization of the growth mechanism and optimization of the deposition process parameters, the $CpZr(NMe_2)_3$–H_2O process was studied using the quartz crystal microbalance (QCM) method. The QCM data were acquired by Q-pod quartz crystal monitor (Inficon). As the variations of the mass sensor temperature markedly influenced the QCM signal, particularly at higher temperatures, the real-time studies were performed only in a T_G range of 70–250 °C. On the basis of these measurements, optimum time parameters of the ALD cycle were determined to be 2, 2, 2, 5 s while the source temperature (T_S) of $CpZr(NMe_2)_3$ was set at 50 °C and the H_2O partial pressure was kept at 27 Pa in the reaction chamber during the H_2O pulse, when the films for post-growth characterization were deposited. The number of deposition cycles was varied from 30 to 1000. For the $ZrCl_4$–H_2O process, T_S of $ZrCl_4$ was set at 140–145 °C while the precursor pulses and purge periods were 2 s each. The parameters of this process were chosen on the basis of earlier QCM studies [11].

All Si(100) substrates used in our experiments were etched in HF to remove native oxide and then rinsed in de-ionized water before loading the substrates into the reactor. Monolayer graphene, which was used as a substrate in some experiments, was grown by chemical vapor deposition (CVD) on commercial 25-μm thick polycrystalline copper foils (99.999%, Alfa Aesar) using a recipe described by van der Zande et al. [19]. The foils were annealed at 950 °C in an in-house built CVD reactor for 60 min in 100/120 sccm flow of Ar/H_2 (both 99.999%, Eesti AGA AS) mixture and then exposed to a 40 sccm flow of the 10% CH_4/Ar (99.999% Eesti AGA AS) gas for about 15 min to obtain graphene. ZrO_2 films were deposited on as-grown graphene in order to avoid unintentional functionalization of graphene that might have taken place during transfer of graphene to other substrates.

2.2. Characterization

X-ray diffractometer (SmartLab, Rigaku™) was used to evaluate the thickness, density and roughness by the X-ray reflection (XRR) and phase composition by grazing incidence X-ray diffraction (GIXRD) analysis methods. The measurements were performed at room temperature using CuKα radiation from a 9 kW X-ray tube with rotating anode. The GIXRD studies were carried out at an incidence angle of 0.30°. Additionally the root mean square (RMS) roughness was measured by the atomic force microscope (AFM) Autoprobe CP II (Veeco Instruments Inc.). The studies were carried out in air using silicon cantilevers with typical tip radius of ≤10 nm. The AFM data were collected from the surface area of 1×1 μm^2 or 5×5 μm^2 in non-contact mode. The RMS surface roughness and the grain size were analyzed by Gwyddion ver. 2.31 software package. Mass thicknesses of the films were measured by the X-ray fluorescence (XRF) analyzer ZSX400 (Rigaku) using the program ZSX Version 5.55 and electron probe microanalysis (EPMA) methods carried out on the JSM-840A and JSM-35CF electron probe microanalyzers (JEOL) [20]. Impurity concentration was determined in the films by the EPMA method [20]. In order to measure the refractive index and obtain additional information on the film thicknesses, we used spectroscopic ellipsometer (SE) GES-5E (SEMILAB–Sopra).

3. Results

3.1. Influence of substrate temperature on growth process

According to QCM studies the self-limited nature of the $CpZr(NMe_2)_3$ adsorption appeared at sufficiently short exposures (2–5 s) already at T_S of 40–50 °C (Figs. 1 and 2). These T_S values were approximately by 100 °C lower than those used in the $ZrCl_4$-based processes [10–12]. Although the film mass did not stabilize completely even during 30 s, it increased relatively slowly after abrupt rise within the first 1–2 s of the $CpZr(NMe_2)_3$ pulse (Fig. 1). The continuous increase of the film mass during the $CpZr(NMe_2)_3$ pulse was the most probably related to the thermal decomposition of the precursor and/or influence of H_2O residues that might have been present in the carrier gas at a level of 10^{-3} Pa approximately. However, the contribution of these effects to the growth rate did not exceed 5% when $CpZr(NMe_2)_3$ pulse durations up to 5 s were used at 250 °C (Fig. 2a).

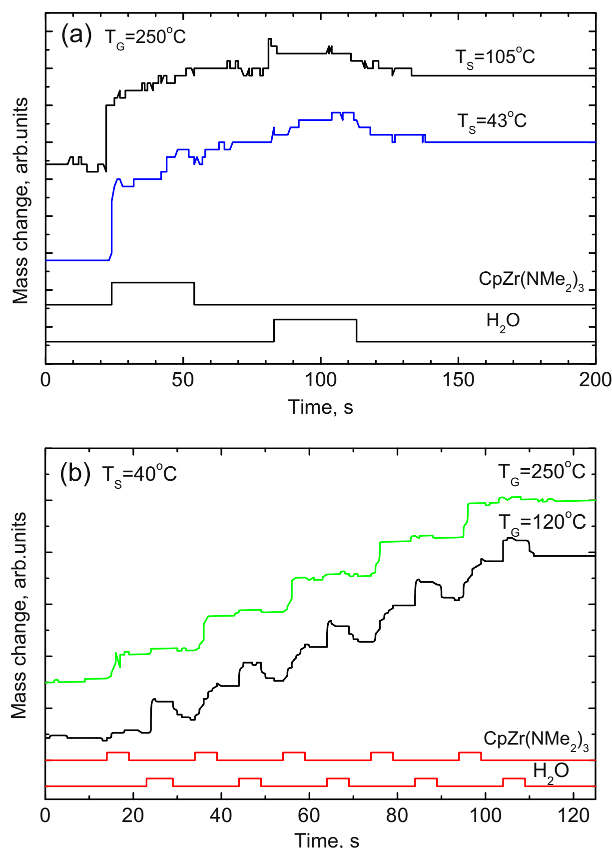

Fig. 1. Film mass recorded by QCM as a function of time (a) at a QCM sensor temperature of 250 °C and at different $CpZr(NMe_2)_3$ source temperatures and (b) at a $CpZr(NMe_2)_3$ source temperature of 40 °C and at different QCM sensor temperatures.

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