



Effect of substrate-enhanced and inhibited growth on atomic layer deposition and properties of aluminum–titanium oxide films



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ABSTRACT

Atomic layer deposition of aluminum–titanium oxide films from different precursor combinations was investigated. In addition to well-known $\text{TiCl}_4\text{-H}_2\text{O}$, $\text{AlCl}_3\text{-H}_2\text{O}$ and $\text{Al}(\text{CH}_3)_3\text{-H}_2\text{O}$ ALD processes, combination of hydrogen-free $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$ processes was used. Most of the films were grown at 350°C because this temperature ensured reliable growth of TiO_2 and Al_2O_3 in all processes combined. The films were deposited using supercycles that contained 1–60 successive cycles for deposition of TiO_2 followed by 1–3 cycles for deposition of Al_2O_3 . The films were amorphous, when 15 or less TiO_2 cycles per Al_2O_3 cycle were applied in a supercycle, and contained anatase when ≥ 30 TiO_2 cycles were applied. A marked increase in the Al deposition per cycle was observed with the increase of the number of TiO_2 cycles per supercycle from 0 to 5–10. With the further increase of the number of TiO_2 cycles from 15 per supercycle to higher values, the Al deposition per cycle depended on the precursor combination used. The Ti deposition per cycle depended, in turn, on the precursor system used for deposition of Al_2O_3 layers. Deposition of Ti was most significantly hindered on Al_2O_3 -rich surface deposited from $\text{AlCl}_3\text{-O}_3$ and markedly enhanced on Al_2O_3 deposited from $\text{Al}(\text{CH}_3)_3\text{-H}_2\text{O}$. In addition, the phase composition markedly influenced the growth rate of both components as well as the mean growth rate and surface roughness of the films.

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1. Introduction

Atomic layer deposition (ALD) is a thin-film preparation technique based on successive self-limited surface reactions allowing deposition of uniform thin films even on substrates with very complex surface profiles [1–5]. Potentially, the method could ensure also a very precise and simple thickness control arising from the dependence of the film thickness on the number of ALD cycles, which contain certain successions of precursor pulses. The dependence of surface reactions on the material and structure of surfaces frequently causes, however, enhancement or inhibition of deposition in the initial stages of ALD [6–8] and leads to marked uncertainty in thickness control, especially in the case of very thin films.

For doping of thin films or deposition of solid solutions in ALD processes, layers of different materials are usually deposited on each other in order to obtain required overall composition of a thin film [4, 5, 9–12]. It is obvious that in this approach, the character of a material growth on another material may significantly influence the mean composition of the film. It has been demonstrated, for instance, that in ALD of Al-doped TiO_2 (ATO) films from titanium tetraisopropoxide (TTIP), trimethylaluminum (TMA) and O_3 at 250°C , the deposition of Al is enhanced and Ti is inhibited compared with the deposition of these elements in ALD of undoped oxides [9]. As a result, the growth of ATO films is slower than the growth of undoped TiO_2 [9] while the Al concentration in the films exceeds the value, which could be expected by

taking into account the ratio of ALD cycles and the growth rates of undoped TiO_2 and Al_2O_3 in corresponding ALD processes. A similar effect has been observed in deposition of ATO films from titanium tetraethoxide, TMA and H_2O [10]. In a very recent study on ALD of ATO [12], we observed even more complex dependence of the Al amount deposited in an $\text{AlCl}_3\text{-O}_3$ ALD cycle on the amount of TiO_2 deposited before applying this cycle. First the Al amount increased with increasing number of $\text{TiCl}_4\text{-O}_3$ ALD cycles applied before the $\text{AlCl}_3\text{-O}_3$ cycle but then started to decrease when the number of $\text{TiCl}_4\text{-O}_3$ cycles exceeded 15. These results demonstrate that processes influencing the composition of solid solutions deposited in ALD processes might be complex and could significantly depend on the precursor combinations used.

The goal of the present paper is to characterize the background of these effects in more detail and, in particular, investigate the influence of precursor combination on the composition of ATO films. The study was stimulated by the results, which had revealed very promising performance of ATO as a high-permittivity dielectric in capacitor structures [4, 11, 13] suitable for dynamic random access memories. Moreover, different combinations of TiO_2 , Al_2O_3 and ATO thin and ultrathin films have several other potential applications ranging from resistive-switching random access memories [14] to optical [15, 16] and anticorrosion coatings [17–19]. In addition to well-known $\text{TiCl}_4\text{-H}_2\text{O}$, $\text{AlCl}_3\text{-H}_2\text{O}$ and TMA- H_2O ALD processes, we characterize combination of hydrogen-free $\text{TiCl}_4\text{-O}_3$ and $\text{AlCl}_3\text{-O}_3$ processes [6, 12, 20, 21], which could have

advantages in applications that require low concentration of residual hydrogen in the films [21–23].

2. Experimental

The films studied in this work were grown in a low-pressure flow-type ALD reactor (Fig. 1) using TiCl_4 together with AlCl_3 or TMA as the metal precursors, H_2O or O_3 as the oxygen precursor and N_2 (99.999%) as the carrier and purge gas. In all cases, an ALD cycle was started with a metal precursor pulse and continued with a purge of the reaction zone with pure carrier gas, oxygen precursor pulse and another purge. In order to obtain sufficient precursor pressures, the AlCl_3 source temperature was set at 100°C while TiCl_4 , TMA and H_2O sources were kept at room temperature ($22 \pm 3^\circ\text{C}$). O_3 was generated from O_2 (99.999%) in a BMT Messtechnik 802N ozone generator. Ozone concentration measured with BMT Messtechnik 964 analyzer at the reactor inlet was $200\text{--}230\text{ g/m}^3$ at the normal pressure. Optimum process time parameters were determined from data of quartz crystal microbalance (QCM) measurements. The precursor pulse durations were chosen to be 0.5 s for TiCl_4 and 2 s for H_2O in the $\text{TiCl}_4\text{--H}_2\text{O}$ process, 2 s for TiCl_4 and 5 s for O_3 in the $\text{TiCl}_4\text{--O}_3$ process, 5 s for AlCl_3 and 2 s for H_2O in the $\text{AlCl}_3\text{--H}_2\text{O}$ process, 3 s for TMA and 2 s for H_2O in the TMA– H_2O process, and 10 s for AlCl_3 and 5 s for O_3 in the $\text{AlCl}_3\text{--O}_3$ process. The purge durations were set at 2 s after each metal precursor pulse and 5 s after the oxygen precursor pulse. In all cases studied, these process time parameters allowed reliable self-limited ALD-type growth of thin films.

The substrate temperature at which the films were grown, T_G , ranged from 150 to 450°C . Most of the experiments were performed, however, with films grown at 350°C . As demonstrated in earlier studies, this temperature ensured ALD of high-quality TiO_2 and Al_2O_3 in all processes combined in this work [2,12,20]. In order to obtain doped films and solid solutions, the films were grown using supercycles that contained 1–60 successive cycles for deposition of TiO_2 followed by 1–3 successive cycles for deposition of Al_2O_3 . Depending on the number of cycles in a supercycle, the number of supercycles was varied from 8 to 750. The total number of cycles applied for deposition of films ranged from 450 to 1550.

The mass thickness and elemental composition of the films were measured by X-ray fluorescence (XRF) spectroscopy method using ZSX400 (Rigaku) spectrometer. From the quantitative amounts of elements determined by XRF, the number of supercycles used for deposition of each film and the number of ALD cycles applied for deposition of each component oxide, the mean amounts of Ti and Al deposited per supercycle and cycle were calculated. For calibration of the measurement procedure, we used binary TiO_2 and Al_2O_3 films with known thicknesses and densities determined by the X-ray reflection (XRR) method. It is worth mentioning that differently from the QCM measurements that could also be used for characterization of mass changes

during the ALD processes [24–29], the XRF data allowed determination of the mass of each element deposited during the film growth. Moreover, at the thicknesses of films studied in this work, the accuracy of the XRF measurements was markedly higher than that of typical QCM studies, especially at deposition temperatures exceeding $200\text{--}250^\circ\text{C}$. Finally, the XRF method is free of artifacts, which are related to uncertainty in determination of surface exchange reactions [28] or etching of the existing film with a precursor supplied [29] and therefore markedly reduce the reliability of the QCM studies.

Grazing incidence X-ray diffraction (XRD) and Raman spectroscopy methods were applied for structure studies while the thickness and surface roughness were determined from XRR patterns. All XRD and XRR studies were carried out on Smartlab (Rigaku) X-ray analyzer using $\text{CuK}\alpha$ radiation. For Raman spectroscopy studies, Renishaw in Via spectrometer was employed. In addition, refractive indices for a series of films with different compositions were determined using GES5E (Sopra-Semilab) spectroscopic ellipsometer.

3. Results and discussion

In order to characterize the growth of component oxides, the surface mass density of elemental Ti and Al deposited in a supercycle and in a cycle were determined using the corresponding amounts of Ti and Al measured by XRF in the films. Figs. 2 and 3 demonstrate that the number of TiO_2 cycles applied in a supercycle significantly influenced the mean amount of Al as well as Ti deposited in a single ALD cycle. The deposition rate of Al as well as the mean deposition rate of Ti was higher on TiO_2 than on Al_2O_3 deposited in AlCl_3 -based processes (Figs. 2 and 3). The results also show that there was no typical nucleation delay in the deposition of TiO_2 after the Al_2O_3 cycle because already in the first TiO_2 cycle, significant deposition rate of Ti was obtained (Fig. 3). During the first 10–15 cycles, however, the deposition of Ti was relatively slow and increased markedly only after applying more than 15 cycles. This kind of effect has been reported for other ALD processes too [8,24,25] and attributed to the transition from amorphous to crystalline growth. Similar explanation can be proposed for the results shown in Figs. 2 and 3. Indeed, the films were amorphous, when the number of TiO_2 cycles applied in a supercycle did not exceed 15 and started to crystallize when ≥ 30 TiO_2 cycles were applied (Fig. 4). An interesting result was that in the initial stage of deposition, the growth rate was lower in the $\text{TiCl}_4\text{--O}_3$ process than in the $\text{TiCl}_4\text{--H}_2\text{O}$ process (Fig. 3) but after applying 30 cycles the deposition rate of Ti in the $\text{TiCl}_4\text{--O}_3$ process became comparable to that obtained in the $\text{TiCl}_4\text{--H}_2\text{O}$ process (Figs. 2 and 3). Thus, crystallization more significantly influenced the growth of TiO_2 from TiCl_4 and O_3 .

The behavior of the TiO_2 deposition from TiCl_4 and H_2O after applying of a TMA– H_2O cycle (Fig. 3) was even more interesting. Unexpectedly high Ti deposition per cycle was obtained in the first TiO_2 cycle.

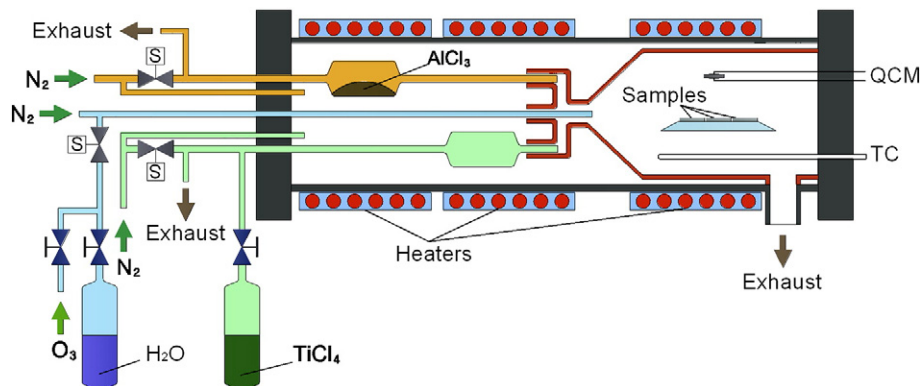


Fig. 1. Schematic layout of ALD reactor set up for deposition of ATO films in $\text{TiCl}_4\text{--O}_3\text{--AlCl}_3\text{--O}_3$ and $\text{TiCl}_4\text{--H}_2\text{O--AlCl}_3\text{--H}_2\text{O}$ processes. For measurement and control of substrate temperatures and for real-time studies of deposition processes thermocouple (TC) and quartz crystal microbalance (QCM), respectively, were applied.

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