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Chemical resistance of thin film materials based on metal oxides grown by atomic layer deposition

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ABSTRACT

Etching rate of technologically important metal oxide thin films in hot sulphuric acid was investigated. The films of Al-, Ti-, Cr-, and Ta-oxides studied were grown by atomic layer deposition (ALD) method on silicon substrates from different precursors in large ranges of growth temperatures (80–900 °C) in order to reveal process parameters that allow deposition of coatings with higher chemical resistance. The results obtained demonstrate that application of processes that yield films with lower concentration of residual impurities as well as crystallization of films in thermal ALD processes leads to significant decrease of etching rate. Crystalline films of materials studied showed etching rates down to values of <5 pm/s.

1. Introduction

Thin films of many inorganic materials, including metal oxides, can be grown by atomic layer deposition (ALD) method [1–3]. ALD has capability to produce pinhole free and highly conformal thin film layers even on complex-shaped objects. Due to application of self-limited surface reactions for material synthesis, the method allows growing layers with well-controlled thickness. For that reason, ALD is implemented in a number of applications [4,5]. Production of flat thin film electroluminescent displays [1,6] and deposition of ultrathin high-k dielectric films of Hf-based compounds [7–11] for the last generations of microelectronic devices [12–15] are just few application examples of the ALD technique. In its development during more than 30 years, atomic layer deposition (known also as atomic layer epitaxy) has shown its usefulness in preparation of thin metal oxide films for chemical sensors [16–19], semiconductor lasers [20], optical coatings [21–27], transparent electrodes [28,29], decorative coatings [27], biocompatible coatings [30], passivating or barrier layers [31,32], and anti-tarnishing [33] or anti-corrosion coatings [34–39] as well.

In several applications listed above, it is substantially important to use thin film materials that are stable in chemically reactive environments. This is of particular significance in the case of materials used in some kinds of sensors, passivating or barrier layers and tarnishing or corrosion preventing coatings. In the latter cases, a native oxide layer formed onto the surface of certain metals like aluminum, titanium, chromium and some other chemically active ones can play the role of a protective coating. These ultrathin and dense oxide layers, often having a thickness of some nanometers, can protect the metals from further oxidation in “normal” conditions but even a small pollution of the environment with aggressive gases, e.g. sulphides and chlorides, together with high humidity level can destroy the native oxide layer and therefore open the metal matrix for further corrosion [40,41]. Even more important is to find alternative methods for protection of some other metals (e.g. iron-based alloys) that can be severely destroyed by corrosion because no natural protection layer is formed on these metals [41].

When using ALD for deposition of protective or other functional coatings, one must be sure that the coating can withstand the conditions in which it will be exploited. Therefore it is important to know the influence of the deposition process parameters, such as precursor combination, substrate temperature, precursor doses, pulse times etc., on the chemical resistivity of real thin film materials.

In literature, one can find data on the etching rates (k_E) of metal oxide films in dry plasma [42–46] or in hydrofluoric acid solutions [47–51]. This kind of information is of particular importance for development of microelectronic technology. Alumina (Al_2O_3) films deposited by plasma enhanced chemical vapor deposition method have been studied for their chemical resistivity in 5% hydrofluoric acid aqueous solution at room temperature [47,48]. The films studied by Catherine et al. [47] were grown from trimethylaluminum ($Al(CH_3)_3$; TMA) and carbon

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dioxide (CO_2) precursors in a temperature range of 25–300 °C and were sufficiently dense and more resistive to the etching when deposited at temperatures ≥250 °C. For instance, k_E was around 15 nm/s for the films deposited at 300 °C. In the work performed by Kim et al. [48], alumina films were deposited on silicon using TMA and dinitrogen oxide (N_2O) as precursors, and He as carrier gas. The films deposited at 120 °C were amorphous and contained a lot of impurities while the films grown at 300 °C had microcrystalline structure of hydrogen-stabilized γ-Al_2O_3 with an O/Al ratio of 1.6 and showed significantly lower etching rates than the films deposited at 120 °C.

In the studies of Bernards et al. [49,50] sol–gel titania (TiO_2) films deposited by spin-coating have been etched in stirred 0.25% HF solution at 25 °C. The etching rate of the films annealed at 150 °C for 30 min was ~0.1 nm/s [50]. With the increase of annealing temperature and, correspondingly, with increasing crystallinity of the films, a decrease of the etching rate of the sol–gel films has been reported [49,50].

Chemical resistivity of metal oxide thin films deposited by ALD has been studied in wet environments only in a limited number of papers [34,52]. Alumina films deposited from $AlCl_3$ and H_2O at 150–400 °C have been etched at 60 °C in acidic (7 M/l H_3PO_4) and in alkaline (0.1 M/l NaOH) aqueous solutions [34]. In addition, titania films deposited from $TiCl_4$ and H_2O at 150–350 °C have been tested with 80% H_2SO_4 at 110 °C [34]. In another work, amorphous alumina films deposited from $Al(CH_3)_3$ and H_2O at temperatures 100–470 °C have been tested in 5% hydrofluoric acid aqueous solution at room temperature [52]. In these studies, it was shown that the resistance to etching increased with the growth temperature (T_G) of the films.

According to earlier data [53] titanium dioxide is insoluble in hydrochloric acid and in dilute sulphuric acid, but it dissolves slowly in hydrofluoric acid and hot concentrated sulphuric acid. Sulphuric acid is known as a strong acid that is used for testing chemical resistivity of different materials, incl. metals and their alloys, which are often coated with natural oxide layers [54,55]. For this reason, the use of sulphuric acid for the chemical resistivity tests of ALD films is of marked interest to find out both, the oxides that can be etched easily and therefore are usable in some lithography processes, and the oxides that are chemically stable even in extremely reactive environments and thereby can be used as high-quality protective anti-corrosion coatings in various environments, e.g. in those containing sulphur trioxide in gaseous form or solved in water.

Thus, in this work, we compare chemical resistance of several metal oxide films by etching those in hot sulphuric acid. Titania, alumina, Ta-oxide (Ta_2O_5) and chromia (Cr_2O_3) thin films, which were studied, were grown by ALD in a wide temperature ranges on silicon substrates from different precursor materials.

2. Experimental details

2.1. Deposition of thin films

The titania, alumina, and tantalum oxide films of 80–380 nm thickness were grown onto Si (1 0 0) substrates by ALD method using a low-pressure flow-type reactor [9] while chromia (Cr_2O_3) films were deposited in another ALD reactor that had optical in-situ monitoring and control system [56]. Before loading into the reactor, the substrates were boiled in a 5:2 mixture of concentrated H_2SO_4 (Sigma-Aldrich) and H_2O_2 followed by rinsing in deionized water, etching the native oxide in HF, and a final rinse in deionized water.

In both reactors used, the precursors were carried to the substrates in flow of N_2 of 99,999% purity (AGA, Linde Group). The carrier gas was also applied for purging the reaction zone between the precursor pulses. The precursors and substrate temperatures used for deposition of the films are listed in Table 1. The details for most of the ALD processes used have been published earlier. Corresponding references [57–62] are also listed in Table 1.

Table 1
Parameters of ALD processes used for preparation the oxide films.

Oxide material	Metal precursor	Oxygen precursor	Growth temperature	References
TiO_2	$TiCl_4$	H_2O	100–300 °C	[57]
TiO_2	TiI_4	H_2O	100–376 °C	[58]
TiO_2	$Ti(OC_3H_7)_4$	H_2O	100–300 °C	[59]
TiO_2	$Ti(OC_3H_7)_4$	H_2O_2	100–300 °C	[59]
TiO_2	$Ti(OC_2H_5)_4$	H_2O	100–350 °C	[60]
Al_2O_3	$AlCl_3$	H_2O	100–900 °C	[52]
Al_2O_3	$Al(CH_3)_3$	H_2O	100–500 °C	This work
Ta_2O_5	$TaCl_5$	H_2O	80–500 °C	[61]
Cr_2O_3	CrO_2Cl_2	CH_3OH	280–465 °C	[62]

An exception is the $Al(CH_3)_3$–H_2O process that has not been described in our earlier publications. In this process, the TMA (Strem Chemicals, 98%) source was kept at room temperature and a needle valve was used to control the flow of TMA vapor into the reactor. Inert gas valving was applied to form the pulses of TMA. The vapor of H_2O that was used as an oxygen precursor was generated from de-ionized water at room temperature. The flow of the H_2O vapor to the reactor was controlled by needle and solenoid valves. The ALD cycle used consisted of expose to TMA for 3 s, purge for 2 s, exposure to H_2O for 2 s and another purge for 5 s.

2.2. Etching and characterization of thin films

Etching of the films was carried out in 80% aqueous solution of sulphuric acid (95–97%; Sigma-Aldrich) at 110 °C by steps with durations of 30–600 s dependently on the evaluated etching rate. Each etching step was followed by rinsing in H_2O. Before the etching process, the thin-film structures were cleaned with RF-plasma in a plasma equipment Femto-1 (Diener) with gas mixture of 20% O_2 + 80% Ar (AGA, Linde Group) for 300 s.

Before and after each etching step the film thicknesses were determined with a precise X-ray fluorescence (XRF) analyzer ZSX400 (Rigaku) having wavelength dispersive X-ray spectrometer. Data of the XRF measurements were quantified to the thin film mass-thickness values with the help of X-ray microanalysis using a thin film analysis procedure [63]. In order to get the physical thickness from mass thickness, density values of the films determined from X-ray reflection measurements were used [64]. Changes in the film topography caused by etching process were studied with an atomic force microscope (AFM) AutoProbe CPII (Park/Veeco), working in non-contact mode and with an environmental scanning electron microscope XL-30 (Philips/FEI).

2.3. Precision of XRF measurements

The films used for the chemical resistance measurements were relatively thin (with thicknesses of 80–380 nm) mainly due to low growth rate of the films in ALD processes. Thus, high precision of the thickness measurements was needed for accurate characterization of the etching rate. To determine the experimental uncertainty of the film thickness measurements by XRF, a series of measurements of Ti K_α radiation intensity of a reference titania film was performed using identical excitation conditions during a period of 5 days. The stability of the sample position in a sample holder and its translation into the measurement chamber as well as stability of X-ray tube, signal detection and counting systems, stabilization time before the measurements, etc. were tested in these studies. The experiments showed that the variations of the Ti K_α radiation intensity values measured for the reference sample did not exceed 2 rel% for a typical measurement cycle that was used for etching rate determination in our experiments.