Atomic Layer Deposition and Chemical Vapor Deposition of Tantalum Oxide by Successive and Simultaneous Pulsing of Tantalum Ethoxide and Tantalum Chloride

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Amorphous Ta_2O_5 films were grown by atomic layer deposition (ALD) or pulsed chemical vapor deposition (CVD) processes as a result of reactions between $Ta(OC_2H_5)_5$ and $TaCl_5$. Pulses of evaporized Ta precursors were led into the reactor successively or simultaneously. H_2O could be applied as a supplementary oxygen source, but the films could be grown also in a water-free process. Films were grown in the temperature range of 275−450 °C. The growth rate of the films obtained by CVD using simultaneous pulsing of precursors exceeded 2.5 times that of the films obtained in the ALD process, where only one metal precursor was applied at a time. The refractive index and permittivity of the films increased with the growth temperature and frequency of Ta precursor pulses, approaching the values characteristic of the films obtained in the conventional ALD or CVD processes.

Introduction

Ta_2O_5 can be used as a thin film dielectric material to increase integration densities in the metal oxide semiconductor field-effect transistors[1] and dynamic random access memories (DRAM) up to the 1 Gbit level.[2,3] The permittivity of amorphous Ta_2O_5 is typically close to 25. Ta_2O_5-based capacitor technologies can be accommodated with the hemispherical-grain-silicon storage node[4] and 300-mm silicon wafer[5] fabrication technologies.

To accommodate a film deposition method with integrated circuit processing, the deposition temperature has to be as low as possible. Ta_2O_5 already can be deposited near room temperature by using a plasma-enhanced metalorganic CVD process.[6] A more common low-temperature CVD route is the pyrolysis and oxidation of tantalum ethoxide, $Ta(OC_2H_5)_5$, above 350 °C.[1] Further, to enhance the CVD rate of Ta_2O_5, active functional groups (OH) can be created, for instance, by dissociating ethanol on the surface of the growing film, thus improving the sticking and chemisorption of $Ta(OC_2H_5)_5$ molecules.[7] This allows one to decrease the CVD temperature below 300 °C. $Ta(OC_2H_5)_5$ is even more active toward the reaction with water and water-assisted CVD can be carried out at temperatures as low as 100 °C.[8]

An alternative low-temperature processing route of Ta_2O_5 is atomic layer deposition, ALD (viz. atomic layer epitaxy), where the solid film grows via successive adsorption and surface reaction cycles between $TaCl_5$ and H_2O[9−11] or between $Ta(OC_2H_5)_5$ and H_2O.[12,13] During one growth cycle in the conventional ALD process, the substrate surface is first exposed to the $TaCl_5$ or $Ta(OC_2H_5)_5$ precursor flux followed by the water pulse. The alternate adsorption cycles of Ta precursor and water are repeated until the target thickness is achieved. Such a surface-controlled growth results in the precise adjustment of the film thickness at the nanometer level,[14,15] accompanied with excellent conformality.[16] The growth temperature of amorphous and smooth Ta_2O_5 films can be decreased at least down to 150 °C in the case of $Ta(OC_2H_5)_5$[12] and even down to 80 °C in the case of $TaCl_5$.[11] The lower limit of the growth

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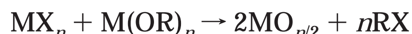
temperature is due to the kinetic activation barrier for the surface reactions. At the same time, increase in the deposition temperature in either of the precursor systems above 275 °C is accompanied by side effects, such as the thermal decomposition of $Ta(OC_2H_5)_5$, resulting in a partial loss in the self-limitation.[12,13] Another side effect is etching of Ta_2O_5 by $TaCl_5$,[10,17] which obviously decreases the film growth rate, degrades film uniformity, and complicates the thickness control.[17]

However, the use of an additional oxygen precursor such as water may oxidize also the substrate surface. This is especially harmful in the case of silicon, where the oxidized surface layer causes a decrement of the overall capacitance. The exploitation of water also may create hydrogen species as defects in silicon.[18] Therefore, water-free processes using oxygen-containing metal precursors are to be developed.[19] However, while pyrolytic single-source processes have been examined in CVD, they cannot be used in ALD.

$Ta(OC_2H_5)_5$ is already an oxygen-containing precursor and might be exploited to deposit Ta_2O_5 films without supplementary oxygen sources. For instance, Ta_2O_5 has recently been grown in a water-free ALD process at 250−280 °C using $Ta(OC_2H_5)_5$ and NH_3 as precursors,[20] although the films contained also nitrogen and consisted, thus, of TaO_xN_y. While making complex oxides by ALD, in some cases it is not necessary to exploit H_2O or another separate precursor for oxygen, but oxygen may come from one of the cation precursors, like in the $CrO_2Cl_2-Al(C_2H_3)_3$ process.[21]

An interesting potential approach for making oxide films is to use two metal compounds, at least one of which is an alkoxide containing oxygen bonded to the metal. This kind of chemistry has been used in sol−gel processes under nonhydrolytic conditions, i.e., in the absence of water, providing the reactions $MX_n + M(OR)_n \rightarrow 2MO_{n/2} + nRX$,



$$MX_n + M(OR)_n \rightarrow 2MO_{n/2} + nRX$$

where M is a metal cation, X is a halide, and R is an alkyl group. The simultaneous application of metal chlorides and alkoxides have formed a basis for a nonhydrolytic, low-rate sol−gel route for several oxide materials such as Nb_2O_5,[22] SiO_2,[23] TiO_2,[24] Al_2O_3[25], or mixed oxides.[26,27] Henceforth, to obtain films with precisely adjustable thickness, morphology and homogeneity, more surface-controlled chemical deposition processes are to be developed. In CVD, the titanium tetraisopropoxide and tetrachloride have been used to obtain nanostructured TiO_2 films, but with the presence of O_2.[28] Recently, we have demonstrated that, besides Ta_2O_5, various oxides including ZrO_2, TiO_2, Al_2O_3, and SiO_2 and their mixtures can be grown by water-free ALD and without any other supplementary oxygen sources.[29]

The purpose of the present study has been a detailed study on the growth of a thin solid film as a result of the reactions between $TaCl_5$ and $Ta(OC_2H_5)_5$. An aim was to develop a novel, reliable, and reproducible film growth process by pulsing $TaCl_5$ into the reactor simultaneously (CVD mode) or alternately (ALD mode) with $Ta(OC_2H_5)_5$.

Experimental Section

Ta_2O_5 films have been grown onto 5 cm × 5 cm Corning 7059 borosilicate glass substrates in a hot-wall flow-type F120 ALCVD reactor (ASM-Microchemistry Ltd.). In this reactor, two substrates are placed together in the susceptor so that their surfaces face each other and form a narrow flow channel of 2 mm width. The precursors evaporated are alternately led to one end of the channel and move in the form of adsorption waves along the substrate surfaces toward the other end. This results in the saturative formation of a monomolecular layer of the respective precursor so that the substrate surfaces become first saturated at their leading edges and, then, also at the trailing edges. The substrate temperature was varied between 250 and 450 °C. Nitrogen was used as a precursor carrier and purge gas. The pressure in the reactor was about 10 mbar. $Ta(OC_2H_5)_5$ (Aldrich) and $TaCl_5$ (Merck) were evaporated from open boats held at 105 and 90 °C, respectively, inside the reactor. To grow a reference sample series by using water as an oxygen source, the water vapor was generated in an external reservoir at room temperature and led into the reactor through needle and solenoid valves.

H_2O, if used, was pulsed only at the end of each reaction cycle after both Ta precursors, not between the Ta precursor pulses, i.e. realizing the pulsing sequence $Ta(OC_2H_5)_5-TaCl_5-H_2O$ or $TaCl_5-Ta(OC_2H_5)_5-H_2O$. The water exposure time was 1.5 s. Pulse times for Ta precursors were varied between 0.2 and 2.0 s. Purge time periods of 0.5 s were used between the precursor pulses in order to avoid gas-phase reactions and to remove the volatile byproducts of surface reactions.

Film thicknesses were calculated using the method described by Ylilammi and Ranta-aho[30] from optical transmission spectra measured by a Hitachi U-2000 spectrophotometer within a wavelength range of 370−1100 nm. Film structure was checked by means of a Philips MPD 1880 powder X-ray diffractometer (XRD) using Cu Kα radiation. The chlorine contamination level was measured by a Link ISIS energy dispersive X-ray spectrometer (EDX) installed to a Zeiss DSM 962 scanning electron microscope. The depth profiling of residual contaminants was carried out using time-of-flight elastic recoil detection analysis (TOF-ERDA) for chlorine and carbon. A 48 MeV I^{9+} beam for TOF-ERDA was obtained from a 5 MV tandem accelerator EGP-10-II at the accelerator laboratory. The TOF-ERDA analysis allowed one to obtain information about the film composition throughout the film thickness, and the residual contents calculated from the composition profile are reported. The light residues such as hydrogen, chlorine, and carbon are well-resolved from each other, and their concentrations as low as 0.1−0.2 atom %, averaged throughout the film thickness, can be determined.

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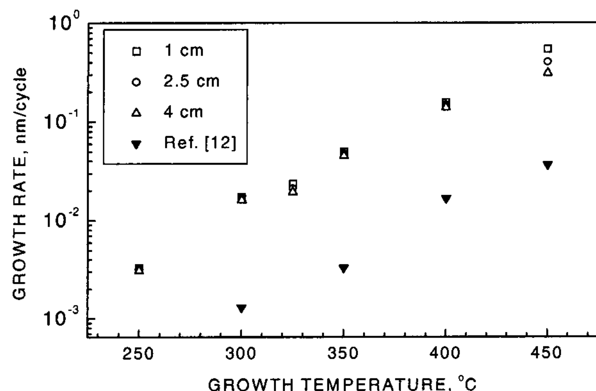

Figure 1. Growth rate of Ta_2O_5 films, grown with the water-free process, versus growth temperature. $Ta(OC_2H_5)_5$ and $TaCl_5$ were pulsed into the reactor simultaneously. Inset values indicate the distance from the leading edge of the substrate, where the film thickness has been measured. Downward triangles show the growth rate in case of pyrolysis of $Ta(OC_2H_5)_5$.

To measure the film capacitance, soda lime glasses covered with an Al_2O_3 ion barrier layer and patterned indium–tin oxide (ITO) electrodes were used as substrates. An array of aluminum electrodes was evaporated onto the film surface, enabling electrical measurements over the substrate area of 10 cm^2, approximately. The effective single electrode area was 12 mm^2. Capacitances were measured at a frequency of 10 kHz using a HP4275A LCR meter. Current–voltage characteristics were recorded using a Keithley 2400 source meter. All the measurements were carried out at room temperature. The films were not heat-treated after the deposition and all the results described below thus characterize the properties of the films in their as-deposited state.

Results

Pulsed CVD Mode. *Film growth.* Earlier it has been shown that, above 275 °C, $Ta(OC_2H_5)_5$ decomposes thermally and the films could be grown already by pulsing only $Ta(OC_2H_5)_5$ without applying intermediate H_2O pulses (Figure 1).[12] Figure 1 also demonstrates the results of the present study, depicting the temperature dependence of the growth rate in the case of the simultaneous pulsing of the Ta precursors. Obviously, the application of $TaCl_5$ in $Ta(OC_2H_5)_5$-based process increases the deposition rate by about an order of magnitude. The deposition proceeds with a considerable rate already at 250 °C.

Figure 2 depicts the thickness profile of the films grown using different pulse lengths. A constant purge time of 0.5 s was applied between the precursor pulses. It is obvious that the most uniform films can be grown with the shortest precursor exposure times. The growth rate tends to be proportional to the length of the precursor pulse. Exceptionally, the growth rate was comparable for the 0.5 and 1.0 s pulse times.

In this process, where the substrate is exposed simultaneously to $TaCl_5$ and $Ta(OC_2H_5)_5$, the growth rate is doubled compared to the conventional ALD process (Figure 3). Conventional ALD is regarded as that proceeding via sequential supply of $Ta(OC_2H_5)_5$ (or $TaCl_5$) and H_2O pulses separated by purge periods. However, the contribution of gas-phase reactions in the case of pulsed CVD mode is, possibly, somewhat increased and the film thickness decreases along the gas flow direction. The thickness uniformity can be improved by exposing the substrate surface to H_2O after the pulse of the Ta precursors. The films grown in the water-assisted process maintain both the high growth rate and uniform thickness characteristic of the process based on simultaneously pulsed Ta precursors and the conventional ALD process, respectively.

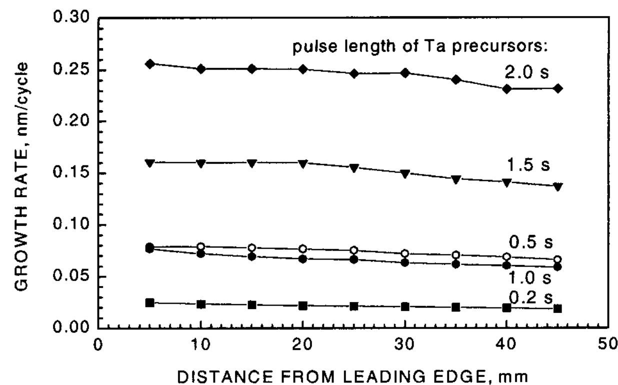

Figure 2. Thickness profiles of Ta_2O_5 films grown with the water-free process with simultaneous pulsing of $Ta(OC_2H_5)_5$ and $TaCl_5$. The parameter varied is the length of the exposure period.

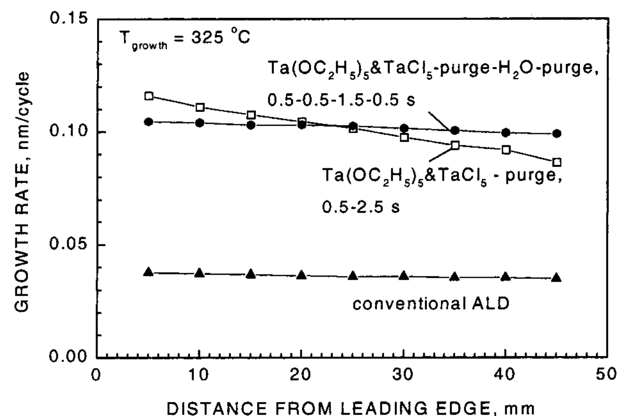

Figure 3. Thickness profiles of Ta_2O_5 films grown with the water-free process with simultaneous pulsing of Ta precursors, compared to the thickness profiles of the films grown in the water-assisted process and conventional ALD process based on alternate exposure of $Ta(OC_2H_5)_5$ and H_2O.

Film Properties. The chlorine content in the films grown by simultaneous pulsing of the Ta precursors decreased from 4 down to 1 atom % with the increase in the growth temperature from 325 to 450 °C. In this particular series, the pulse length of the Ta precursors was chosen as 0.2 s, i.e as short as possible. The residual contamination in the films grown at 325 °C was weakly correlated to the pulse length of the Ta precursors, while the chlorine content could be decreased down to 2 atom % in the films grown with the pulse length of 2.0 s. The purge period was kept constant at 0.5 s. When the purge period was increased up to 2.5 s, the chlorine content remained low at the 2–3 atom % level. In the film grown using similar parameters but in the water-assisted process, the chlorine content decreased, remarkably, down to 0.2 atom %. Regarding the chlorine content, the results of the EDX and TOF-ERDA measurements were comparable. In accord with the TOF-ERDA results, all the contaminants, C, H and Cl, are present but at equally low levels. The carbon and hydrogen contents were comparable to or lower than the chlorine content

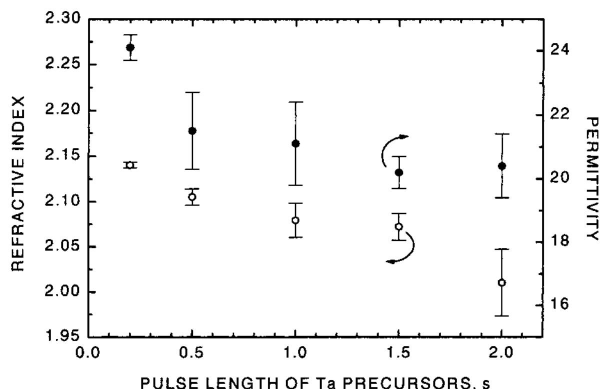

Figure 4. Refractive index and permittivity of Ta_2O_5 films, grown with the water-free process at 325 °C, versus Ta precursor exposure time. $Ta(OC_2H_5)_5$ and $TaCl_5$ were pulsed into the reactor simultaneously.

in all the films studied, below the 1 atom % level. All the films grown were amorphous.

The dielectric properties of the films approached those characterizing the films grown in the conventional water-based ALD process. The permittivity and refractive index of amorphous or moderately crystallized ALD films deposited earlier reached 23−25[12,31] and 2.20−2.23,[11,12,31] respectively. In the films grown in the water-free CVD-like process at 325 °C, the average refractive index as well as its lateral uniformity decreased with the increasing length of the Ta precursors pulse (Figure 4). The same behavior was observed for the permittivity value (Figure 4). The growth temperature did not have any obvious effect on the refractive index when the shortest pulse time of 0.2 s was applied. At the same time, the refractive index decreased from 2.14 down to 2.07 when the precursor pulse length was increased from 0.2 to 1.5 s. Also the length of the purge period influenced the refractive index value. The refractive index increased from 2.10 to 2.20 when the purge period was increased from 0.5 to 2.5 s, while the precursor pulse length was kept constant at 0.5 s. Obviously, the higher the purge time to pulse time ratio, the higher the refractive index.

For the water-assisted process based on the simultaneous pulsing of the two Ta precursors, refractive index and permittivity as high as 2.21 and 25, respectively, were measured for the films grown at 325 °C. These values are similar to those measured for the films fabricated in the conventional $TaCl_5-H_2O$[11,31] and $Ta(OC_2H_5)_5-H_2O$[12,14] ALD processes.

ALD mode. *Film Growth.* In the ALD process, the substrate surface was alternately exposed to the different Ta precursor fluxes. At first, relatively short $TaCl_5$ and longer $Ta(OC_2H_5)_5$ pulses were supplied, first adsorbing a molecular layer of $TaCl_5$ followed by exposing the substrate surface to the $Ta(OC_2H_5)_5$ flow and surface reaction occurring between $TaCl_5$ and $Ta(OC_2H_5)_5$. The fluxes of the two Ta precursors were separated by very short purge times of 0.2 s length. This surface reaction step was followed by a relatively long purge time of 1.0 s. For another series of samples, the sequence of the Ta precursor pulses was changed. In the process with sequential pulsing, the film growth

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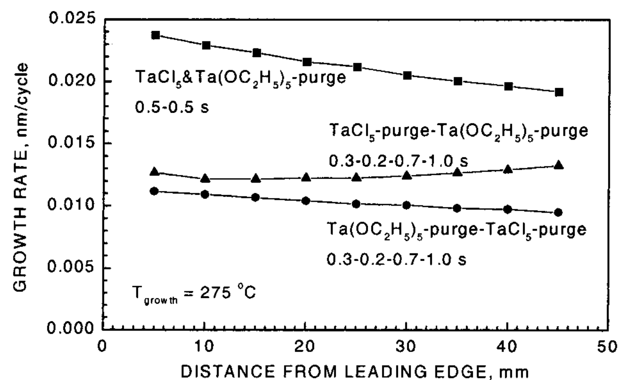


Figure 5. Thickness profiles of Ta_2O_5 films, grown at 275 °C with the water-free process using different sequences of Ta precursor pulses.

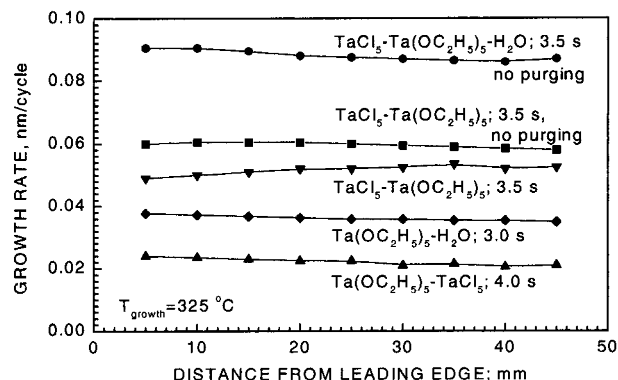


Figure 6. Thickness profiles of Ta_2O_5 films, grown at 325 °C with the water-free ALD process using different sequences of Ta precursor pulses. The labels indicate the sequence of the precursors in the deposition cycle as well as the total time consumed by one cycle. For comparison, profiles for the films grown in the water-assisted process are given (the first and the fourth curve from the top).

rates calculated per cycle as well as the absolute growth rate calculated per time unit were considerably lower than in the process using simultaneous pulsing (Figure 5). However, the thickness of the films grown from the alternately pulsed precursors was more uniform compared to the films grown by simultaneous pulsing. There was also a difference in the nature of the thickness profile: the film thickness decreased toward the trailing edge of the substrate when the $Ta(OC_2H_5)_5$ pulse was applied first and was followed by the $TaCl_5$ pulse. When $TaCl_5$ was applied first, the thickness profile became inverted, showing an increase in the growth rate toward trailing edge (Figure 5).

Figure 6 demonstrates the thickness uniformity of the films grown at 325 °C. From the two lowest profile curves, it becomes obvious that the conventional $Ta(OC_2H_5)_5-H_2O$ ALD process results in higher growth rate than the new, water-free $Ta(OC_2H_5)_5-TaCl_5$ process. Analogously to the growth proceeding at 275 °C, described above (Figure 5), the growth rate was increased when pulsing $TaCl_5$ before $Ta(OC_2H_5)_5$. In this case (the middle profile curve in Figure 6), the growth rate already exceeds that in the conventional ALD. The growth rate can be increased further by minimizing the purge time between the precursor pulses. In this case the purge time was established only by the time delay caused by the finite switching rate of solenoid valves and the carrier gas flow rate. Even higher growth rates

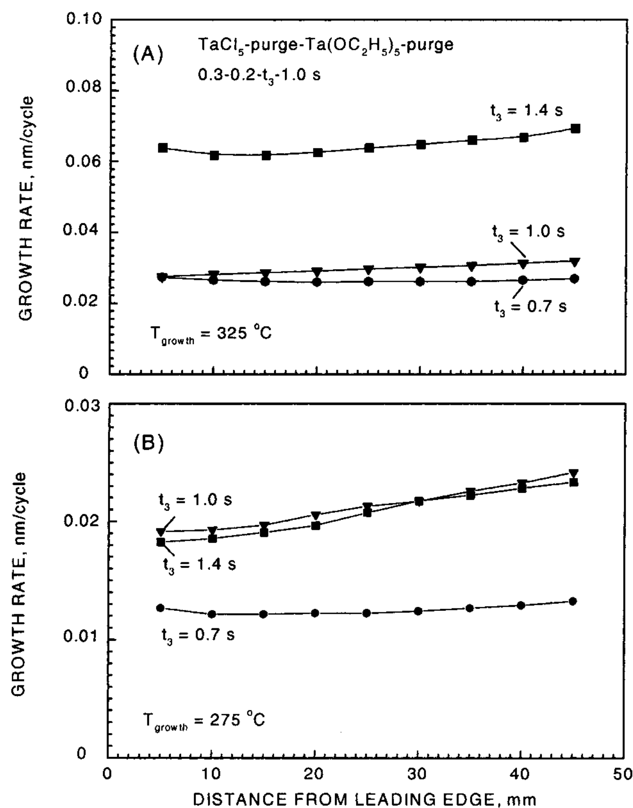


Figure 7. Thickness profiles of Ta_2O_5 films, grown at 325 °C (A) and 275 °C (B) with the water-free process by successive pulsing of $TaCl_5$ and $Ta(OC_2H_5)_5$. The parameter varied was the pulse length for $Ta(OC_2H_5)_5$.

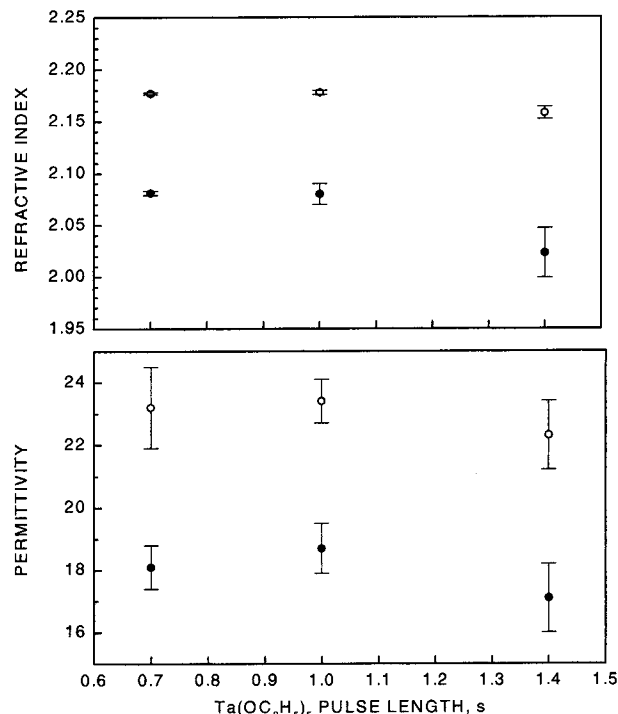


Figure 8. Dependence of refractive index and permittivity of Ta_2O_5 films on $Ta(OC_2H_5)_5$ pulse length. The films were grown at 325 °C (open circles) and 275 °C (closed circles) with the water-free process via successive pulsing of $TaCl_5$ and $Ta(OC_2H_5)_5$.

can be achieved when completing the Ta_2O_5 formation by applying water pulses after the two sequential Ta precursor pulses, as shown by the upmost profile curve in the Figure 6.

The pulsing sequence where the $Ta(OC_2H_5)_5$ pulse was applied after the relatively short $TaCl_5$ pulse resulted in higher growth rates. For this reason, the effect of the $Ta(OC_2H_5)_5$ pulse length was studied in some more detail. At 275 °C, the $Ta(OC_2H_5)_5$ exposure time as short as 0.7 s resulted in films of relatively uniform thickness (Figure 7) growing with rather moderate rate. Prolongation of the $Ta(OC_2H_5)_5$ exposure time above 1.0 s increased the growth rate. However, also the thickness nonuniformity was increased. Differently from the process at 275 °C, the growth rate at 325 °C did not increase when the exposure time was increased to 1.0 s (Figure 7). Upon further prolongation of the $Ta(OC_2H_5)_5$ exposure up to 1.4 s, the growth rate increased remarkably, however.

Film Properties. In the films grown by using the alternate precursor pulsing, the contamination level was obviously dependent on the temperature. The chlorine content in the films grown at 275 °C was about 6 atom %. In the films grown at 325 °C, the chlorine content was decreased down to 2 atom %. The chlorine content was not affected by the precursor pulse length. Also the variations in the dielectric properties could not be clearly correlated to the chlorine contamination level. Thus, the chlorine content in the films grown by the water-free process with alternate precursor pulsing (2 atom %, appr) was somewhat lower than in the water-free process with simultaneous pulsing (4 atom %, appr), in accord with both EDX and TOF-ERDA results. The hydrogen and carbon contents remained low, below 1 atom %, in all the films studied. All the films grown were amorphous.

The dielectric properties of the films deposited at 325 °C were better than those of the films grown at 275 °C. Figure 8 shows the dependence of the refractive index and permittivity on the $Ta(OC_2H_5)_5$ exposure time and growth temperature. It is obvious that the increase in the deposition temperature increases the quality of the films. In addition, shorter exposure times are preferable. The alternate and simultaneous pulsing modes for $TaCl_5$ and $Ta(OC_2H_5)_5$ resulted in films with rather similar dielectric properties. The permittivity and refractive index values attained in both water-free and water-assisted depositions were comparable to those characterizing films grown in conventional $Ta(OC_2H_5)_5-H_2O$[12,14] or $TaCl_5-H_2O$[12,31] ALD processes. Furthermore, Figure 9 demonstrates that also the leakage current levels in the films deposited using different process chemistries are comparable.

Discussion

It is known from solution studies that reactions between metal halides and alkoxides lead to the formation of metal−oxygen−metal bridges by thermally activated condensation between halide and alkoxide groups.[26] An alkoxy group of one precursor molecule coordinates via its oxygen atom to the metal center of a second metal halide molecule. The simultaneous nucleophilic attack of chloride on the carbon bound to oxygen favors the relatively easy cleavage of the oxygen−carbon bond.[23] These reactions lead to the formation of alkyl halides. The reactions proceed until completion,

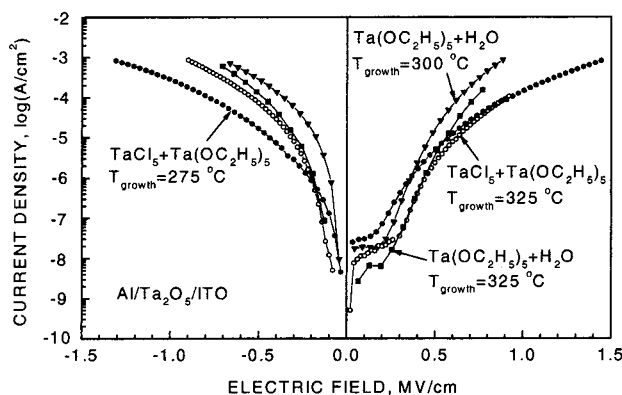
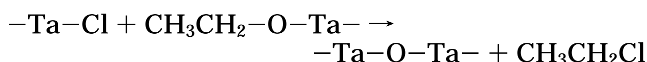


Figure 9. Leakage current density of the Ta_2O_5 films grown at different temperatures using conventional $Ta(OC_2H_5)_5-H_2O$ and water-free $Ta(OC_2H_5)_5-TaCl_5$ ALD processes. Polarity is expressed as the voltage applied to the Al electrode in relation to ITO.

provided the reaction products are removed from the system.[23]

These nonhydrolytic reactions are slow at the temperatures below 110 °C usually applied in sol–gel processes.[26,27] However, along with the thermal cleavage of bonds in metal alkoxides at the temperatures used in the ALD process described above, the reactions can be accelerated. Thus, in the growth processes investigated in the present study, the nonhydrolytic reactions are promoted either in the gas phase (simultaneous pulsing) or on the substrate (alternate or simultaneous pulsing) in accord with the following simplified scheme:



$$-Ta-Cl + CH_3CH_2-O-Ta- \rightarrow -Ta-O-Ta- + CH_3CH_2Cl$$

This should result in the formation of oxygen bridges between adjacent Ta atoms and, eventually, the formation of Ta_2O_5.

Another favored reaction taking place and competing with the condensation mechanism, at least in solutions, is the redistribution of ligands leading to the mixture of halogenoalkoxides.[26,27] This is also a possible source for residual contamination, which tends to be higher at lower growth temperature, where the condensation is assumptionally less completed. The reactions may proceed with finite, even rather slow, rate, and thus time is needed for completion and better removal of the reaction products. A moderate, but observable, dependence of the films purity on the longer purging time described above confirms the slow removal of side products of surface reactions.

These two processes, where the precursors are led into the reactor simultaneously or separately, can be distinguished also on the basis of their different thickness profile. The simultaneous supply of the Ta precursors results in films with thickness monotonically decreasing toward the trailing edge of the substrate (Figure 5). Such a thickness profile can often be observed in CVD processes and in those ALD processes where some overlap between the precursor fluxes can be considered, due to their insufficient separation in time. In this case, the significance of the surface control in the adsorption/growth process is reduced. During the alternate pulsing of the Ta precursors, the finite receiving capability of the surface enables the adsorption of a single monolayer only, limits the absolute growth rate, and causes thickness profiles more characteristic of the conventional ALD processes. The film thickness increases toward the trailing edge of the substrate when the $TaCl_5$ pulse is introduced after the relatively long (1.0 s) purge following the adsorption of $Ta(OC_2H_5)_5$ (Figure 5). A possible explanation for the tendency toward inverted profiles may be the etching of Ta_2O_5 by $TaCl_5$ which at these temperatures is relatively weak.[10] The etching effect may still be stronger when $TaCl_5$ flux arrives onto the surface of amorphous Ta_2O_5. The amorphous Ta_2O_5 is assumptionally formed during the relatively long purge period after reacting the chemisorbed ($-TaCl_x$) species with $Ta(OC_2H_5)_5$. The formation of oxide may at this temperature be somewhat enhanced by thermal decomposition of $Ta(OC_2H_5)_5$. At the same time, the etching effect seems not to be apparent when the $TaCl_5$ is immediately reacted with the ($-Ta(OC_2H_5)_x$) terminated surface. In this case, the etching activity of $TaCl_5$ is likely consumed in the surface reaction with ethoxo groups. An analogous relation between thickness profile and the sequence of Ta precursors may be observed also at 325 °C.

Properties, like thickness uniformity and its dependence on the amount of pulses, of the films grown may be regarded as those commonly characterizing the ALD growth mode. However, some ALD features such as self-limiting adsorption and formation of monomolecular layer are hardly observable. This is first caused by the side effects characterizing the particular Ta precursors. At 275 °C, $Ta(OC_2H_5)_5$ already starts to decompose[12,13] while $TaCl_5$ begins to etch the underlying amorphous film. Nevertheless, as the decomposition and etching processes are rather slow, the film thickness remains precisely determined by the amount of deposition cycles, while the thickness uniformity remains ensured by the limited receiving capability of the surface.

The substrate temperature is the major factor affecting the growth rate and film quality. The surface reactions between $TaCl_5$ and $Ta(OC_2H_5)_5$ at 325 °C are considerably faster than at 275 °C. For this reason, moderate changes in the $Ta(OC_2H_5)_5$ exposure periods from 0.7 to 1.0 s do not affect the growth rate remarkably (Figure 7). At the same time, longer time is needed at 275 °C to complete the surface reactions between $TaCl_5$ and $Ta(OC_2H_5)_5$. Therefore, an increase in pulse length results in significant increase in growth rates, probably until the pulse time becomes long enough to saturate the surface with reacted species and the process becomes self-limited. The pulse time of 1.4 s results at 275 °C in the same growth rate as observed in the case of 1.0 s at 325 °C (Figure 7.). At 275 °C, the effect of thermal decomposition of $Ta(OC_2H_5)_5$ is still weak and does not cause a remarkable increase in the deposition rate upon further prolongation of the exposure time. At 325 °C, however, the effect of thermal decomposition is considerably stronger. The surface reactions between the adsorbed ($-TaCl_x$) species and the oncoming $Ta(OC_2H_5)_5$ become completed already during the first second of the exposure time, approximately, and the growth rate further increases largely due to the decomposition of $Ta(OC_2H_5)_5$. This increases the overall growth rate above 0.06 nm/cycle when an exposure period as long as 1.4 s is applied (Figure 7).

Higher growth rates or improved thickness uniformity can be attained by using water as a supplementary oxygen precursor after each pulse of the simultaneously introduced Ta precursors (Figure 3) or after each sequence of the successively adsorbing Ta precursor (Figure 6). Water probably activates the freshly formed Ta_2O_5 surface covering it uniformly with OH groups, acting as reactive adsorption sites for the subsequent Ta precursor exposure. This is likely the main factor improving the film uniformity. The effect seems to be pronounced in the process with simultaneous pulsing of the Ta precursors. In this case the intemediate water pulsing improves the film uniformity but does not influence the average growth rate (Figure 3). The application of water also completes the surface reactions, decreasing the amount of residual chlorine. In case of the alternate Ta precursor pulsing, water enhances also the growth rate noticeably (Figure 6), while the thickness profile is not affected. The film thickness, in the latter case, is quite uniform already without water pulsing.

The dielectric properties of the films deposited at 325 °C were somewhat better than those of the films grown at 275 °C (Figure 8). This is likely due to the higher residual content accompanying the lower density of the films formed at 275 °C. The refractive index of the films can be correlated to the film density which, in turn, depends on the contamination level. The moderate increase in residual content, however, does not affect considerably the film resistivity, as the films grown at different temperatures and using different process chemistry demonstrate similar leakage (Figure 9). Due to the Al−Ta_2O_5−ITO capacitor structures used, the current−voltage curves were nonsymmetric with respect to the polarity of electrodes. However, the shape of the curves was essentially the same for the films deposited with the different processes, allowing one to rely on the similar nature of interface quality and conduction mechanisms.

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