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Enhanced growth rate in atomic layer epitaxy deposition of magnesium oxide thin films

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Thin films of MgO were deposited by atomic layer epitaxy (ALE) from bis(cyclopentadienyl)magnesium and water using soda lime glass and Si(100) as substrates. Deposition parameters were studied in the temperature range of 100–400 °C. A plateau of surface-controlled growth was observed at 200–300 °C with a growth rate of 1.16 Å cycle^{-1} on both substrates which is almost a magnitude higher than the ALE growth rate obtained with β-diketonate-type precursors and ozone or hydrogen peroxide. The growth was studied in more detail at 300 °C to confirm the surface-controlled nature of the deposition process. The MgO films obtained were analysed by time-of-flight elastic recoil detection analysis (TOF-ERDA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscopy (AFM) to determine chemical composition, crystallinity and crystallite orientation as well as surface morphology. Films deposited below 200 °C were amorphous but above that polycrystalline with (111) dominant orientation on both substrates. According to XPS and TOF-ERDA measurements the films were stoichiometric when deposited at 200–400 °C. Impurity levels of 0.1 at% for carbon and 0.5 at% for hydrogen were detected by TOF-ERDA when films were deposited at 300 °C. Film roughness was dependent on the deposition temperature. Deposition carried out at 250–350 °C produced films with rms values of 8–10 nm whereas the roughness of films deposited above or below this temperature range was 2–4 nm.

Introduction

Atomic layer epitaxy (ALE), also referred to as atomic layer deposition (ALD), has been successfully employed for the deposition of magnesium oxide thin films from the β-diketonate-type precursor (Mg(thd)$_2$) and ozone (thd = 2,2,6,6-tetramethylheptane-3,5-dione).[1] Hydrogen peroxide has also been used as an oxidizer but this process suffers from the low reactivity of Mg(thd)$_2$ with H_2O_2 leading to a relatively high deposition temperature where the Mg-precursor partially decomposes.[2] Furthermore, the use of this type of bulky precursors, which in the case of Mg(thd)$_2$ even has a dimeric structure,[2] leads to a low growth rate due to steric hindrance during the chemisorbed state on the substrate. At temperatures in the region of 300–450 °C, both oxidizers yield a similar growth rate of around 0.1–0.15 Å cycle^{-1} without a self-limiting ALE mechanism but rather resembling a pulsed CVD-type growth. Below 300 °C the growth rate of Mg(thd)$_2$/H_2O_2 was not reported and presumably no film was obtained.[2] Due to the higher reactivity of ozone a self-limiting growth was obtained at 225–250 °C with a growth rate of 0.27 Å cycle^{-1} on a glass substrate.[1] An obvious problem in view of a possible industrial application is the narrow 'ALE window' observed, *i.e.* the temperature range where the reaction is surface controlled is limited when ozone is used as an oxidizer.[1] Furthermore, possible carbon impurities from incomplete removal of the bulky ligands may impair the quality of the film. Carbon content may rise to significant levels when the deposition temperature is low or when a mild oxidizer such as water or oxygen is used. By selecting a less bulky and more reactive precursor it would be possible to enhance the growth rate and reduce the carbon content of the films.

True metal–organic compounds possessing a metal–carbon bond, such as bis(cyclopentadienyl)magnesium (($C_5H_5)_2Mg$), are volatile but at the same time sensitive to air and moisture. However, $(C_5H_5)_2Mg$ is commercially available and has been used in MOCVD as a precursor for p-type doping of semiconductor materials (GaN,[3–5] AlGaN,[6] InGaAlP,[7] InP[8]). $(C_5H_5)_2Mg$ has also been reported as a precursor for depositing MgO thin films by an ALE-related process at 500–900 °C.[9,10] However, it is obvious that at these high temperatures the deposition takes place by partially decomposed species of $(C_5H_5)_2Mg$ or by a pyrolytic mode as seen by the higher growth rates obtained.[10]

Here we report our studies on self-limiting ALE deposition of MgO thin films by using $(C_5H_5)_2Mg$ and H_2O as reactants in an attempt to enhance the growth rate.

Experimental

MgO thin films were deposited in a commercial MC-120 ALE reactor manufactured by Microchemistry Ltd.[11] Sequential pulsing of source materials was carried out by inert gas valving and using pure nitrogen (99.9999%) as a carrier and purging gas. Bis(cyclopentadienyl)magnesium (Morton International, no. 19612) and distilled water were used as reactants. Based on vapor pressure data,[12] an external cylinder of $(C_5H_5)_2Mg$ was heated to 50 °C. The precursor vapor was transported through heated lines into the reactor by 60 cm^3 min^{-1} N_2 flow. Water vapor was generated in a cylinder kept at 30 °C without the use of an additional bubbling system. The films were deposited onto 5 × 10 cm^2 soda lime glass and Si(100) substrates at 100–400 °C.

MgO thin film thicknesses were measured by profilometry (Sloan Dektak 3030ST from Veeco Instruments) from steps etched by dilute HCl. Thicknesses were also determined by fitting the optical spectra[13] which, in reflectance or transmittance mode, were recorded by a Hitachi U-2000 spectrophotometer in the region of 190–1100 nm for silicon substrates and 370–1100 nm for soda lime glass substrates. The crystallite orientation of thin films was determined by recording the XRD

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diagrams in a Philips MPD 1880 powder diffractometer using Cu-Kα radiation. Surface morphologies of the films were examined by a Nanoscope III atomic force microscope (Digital Instruments) using a scanning area of 2 × 2 μm^2. Samples were measured in tapping mode and scanning frequency of 1–2 Hz was used.

The depth profiling of MgO thin films was carried out using time-of-flight elastic recoil detection analysis (TOF-ERDA).[14] In this ion beam analysis method usually heavy ions are used as projectiles which hit the sample and generate forward recoiling sample atoms. For each recoil the velocity and energy are determined using timing gates and a charged particle detector, respectively. By the use of these two signals different masses can be separated. The heavy recoil energy spectra are obtained from the TOF signals but for hydrogen the charged particle detector signal is used. Using a known measurement geometry, stopping powers and scattering cross sections depth profiles are deduced for each element. In this study the sample surface was tilted 20° and recoils were detected at 40° with respect to the incoming beam. The 53 MeV $^{127}\mathrm{I}^{10+}$ beam used for the TOF-ERDA was obtained from a 5 MV tandem accelerator EGP-10-II at the Accelerator Laboratory of the University of Helsinki.

XPS measurements were carried out at the HUT Center for Chemical Analysis. MgO thin films were analysed using AXIS 165 by Kratos Analytical with monochromated Al-Kα irradiation at 100 W. Air-exposed samples were measured as received without further cleaning. Samples were analysed at three points with an analysis area of less than 1 mm^2. Wide scans were acquired using 80 eV analyser pass energy and a 1 eV step and high resolution spectra of the C 1s, Mg 2p and O 1s regions were recorded using a 20 eV analyser pass energy and 0.1 eV steps. Binding energies in high resolution spectra, shifted due to neutralization of the insulating specimen,[15] were corrected using the C 1s line as an internal standard.

Results and discussion

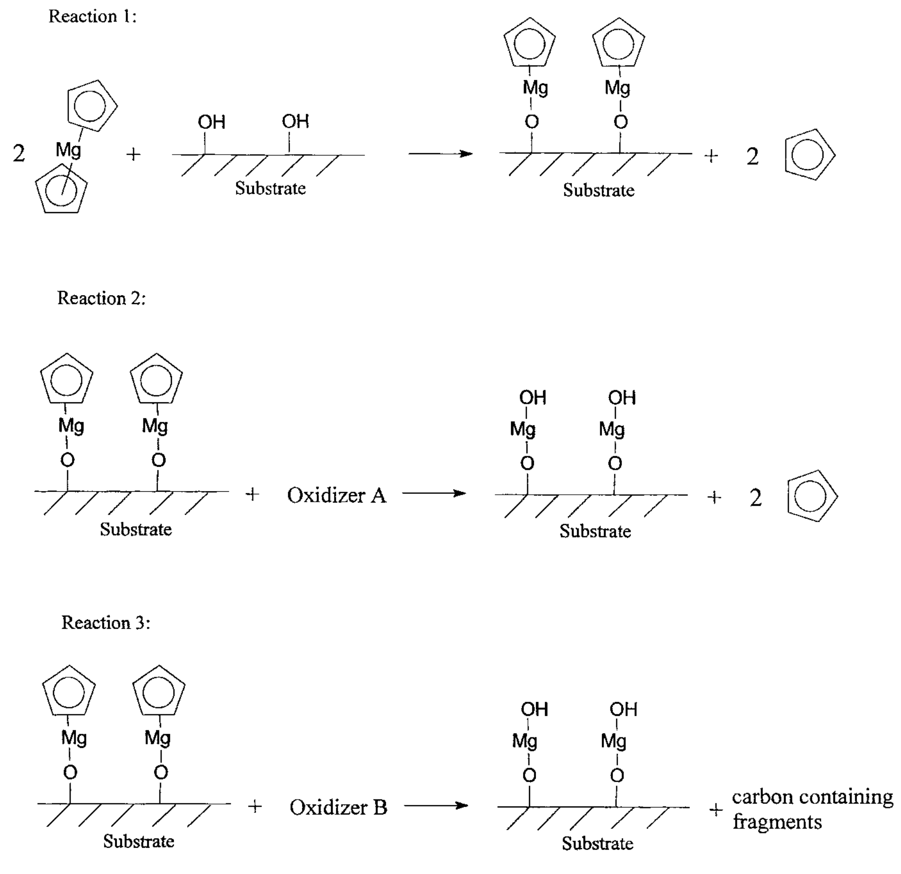
Reactions of gaseous $(C_5H_5)_2Mg$ with a hydroxy terminated surface have been previously investigated.[16] It was observed that the magnesium compound reacts quantitatively with the OH groups of silica producing Si–O–Mg(C_5H_5) surface species. This kind of mechanism may also be dominant in the case of other oxide substrates (Scheme 1, reaction 1).

Oxidizers of the cyclopentadienyl precursors can be divided into two different categories. Mild oxidizers (A-type) break only the metal–carbon bond (Scheme 1, reaction 2) while with strong oxidizers (B-type) the C_5H_5-ligand is completely decomposed (Scheme 1, reaction 3) leading to carbon contamination. Typically water has been used as oxidizer in the organometallic case because of the relative weakness of the metal–carbon bond as exemplified by $Al(CH_3)_3$.[17]

For the $(C_5H_5)_2Mg$ precursor the possible oxidizing reactions can thus by written as follows (reactions 2 and 3).

Especially in the case of cyclopentadienyl derivatives attention should be paid to select a relatively weak oxidizer that only breaks the metal–carbon bond and leaves the cyclopentadienyl ring intact, thus preventing carbon impurities getting into the film. In our preliminary studies we searched for a suitable oxidizer for $(C_5H_5)_2Mg$ at 300 °C. When oxygen or air was used as a B-type oxidizer, it was observed that the deposited films were brownish black indicating the presence of carbon impurities in the film. In contrast, when water was used as oxidizer, the deposited films were clear and transparent. By using water as oxidizer, the transmittance of 150 nm MgO film at 555 nm was 88–90% while the soda lime glass used as substrate has a transmittance of 92%.

In order to determine the surface-controlled deposition region for MgO thin films, the growth rate of MgO thin films was studied as a function of deposition temperature. First, the reactant pulse length was selected so that a complete surface saturation was obtained. The effect of the deposition



Scheme 1

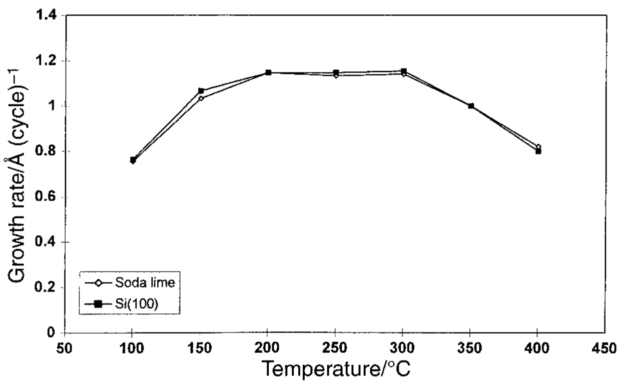


Fig. 1 Deposition rate of MgO thin films on soda lime and Si(100) substrates as a function of temperature. Thicknesses were measured at 4 cm from the leading edge. Source temperature was 50 °C, $(C_5H_5)_2Mg$ and H_2O pulse times were 1.0 s and 0.5 s, respectively.

temperature was then investigated while keeping the other parameters constant. After the deposition the film thicknesses were measured from four spots in the middle of the substrate along the flow direction. Below 200 °C the deposition rate was lower but even at 100 °C it was 0.76 Å cycle^{-1}. A plateau in the growth rate was observed at 200–300 °C where the deposition rate of 1.16 Å cycle^{-1} was obtained with both substrates. Depositions carried out at higher temperatures, *viz.* 350 and 400 °C, resulted in growth rates of 1.0 and 0.7 Å cycle^{-1}, respectively (Fig. 1). Adhesion of the films was tested by the tape test.[18] No peeling was observed regardless of the substrate or the deposition temperature. The overall lowering of the growth rate at temperatures over 300 °C is most likely due to decomposition of the $(C_5H_5)_2Mg$ together with a decrease in the number of surface hydroxy groups acting as reactive sites. Similar phenomena have been observed in the case of Al_2O_3 deposition from organometallic precursors. It is interesting to note that, in contrast to our previous studies on ALE deposition of MgO from β-diketonate-type precursors, the substrate had no effect on the growth rate. In the case of $Mg(thd)_2$ the growth rate of MgO on a silicon substrate was 20% lower than that on a soda lime substrate.[1]

The magnesium to oxygen ratio as well as the possible impurities were analyzed by TOF-ERDA. Depositions carried out at 200–400 °C resulted in stoichiometric MgO films (Fig. 2). This temperature region is slightly wider than the actual ALE window and a slight increase in carbon content was observed when the deposition temperature was above 300 °C. It is noteworthy that the depositions below 200 °C resulted in an increase in both carbon and hydrogen content. Low deposition temperature together with water produced $Mg(OH)_2$ resulting in off-stoichiometry of the films with respect to the ideal 1 : 1 ratio in MgO. During heavy ion irradiation in ERDA a loss of hydrogen can be observed during measurement. To avoid misinterpretations only those events are used for the analysis where hydrogen stays fully in the sample. In the analysis hydrogen and carbon surface contamination was neglected. The surface roughness effects upon the ERDA results were approximated to be minimal.

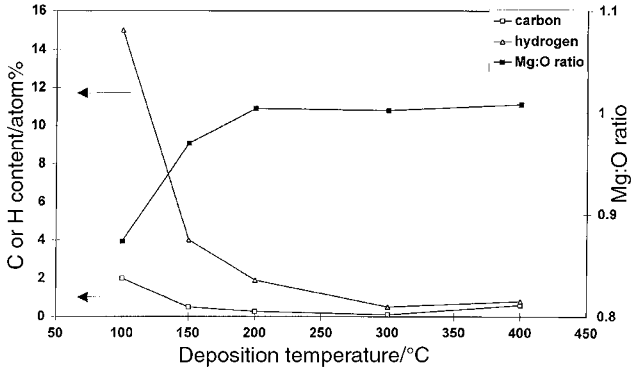


Fig. 2 Mg : O stoichiometry as well as carbon and hydrogen contents in ALE-deposited MgO films as a function of deposition temperature as determined by TOF-ERDA. Measurements were carried out for films deposited onto Si(100) with a thickness of 100–170 nm.

ALE type growth was verified by changing the reactant pulse times. It was observed that for $(C_5H_5)_2Mg$ pulsing times under 1.5 s were too short to obtain surface saturation over the whole substrate area when a 60 cm^3 min^{-1} flow of N_2 carrier gas was used (Fig. 3). In this case uniform films were obtained by longer precursor pulse times. A similar result could also be obtained by increasing the N_2 carrier gas flow rate through the Mg-precursor container. Pulsing times from 1.5 to 3.0 s resulted in the same growth rate indicating surface saturation and the absence of uncontrolled decomposition of $(C_5H_5)_2Mg$. Pulsing times of H_2O were similarly studied from 0–2.5 s. As expected, no film was obtained by pulsing $(C_5H_5)_2Mg$ alone indicating that the precursor was stable without any gas phase decomposition. When using water pulses longer than 0.5 s, the growth rate remained constant leading to uniform films over the whole substrate area. Furthermore, the thickness of the MgO film as a function of the number of deposition cycles was investigated at 300 °C. A typical feature in an ALE process is that the film thickness is controlled by the number of deposition cycles. Also in this case, the MgO growth rate *vs.* the number of cycles was perfectly linear on both substrates indicating a surface controlled process.

XRD measurements showed that the films deposited above 200 °C were polycrystalline cubic MgO. Only the (111) reflection of MgO was observed regardless of the substrate (Fig. 4). Intensities of the reflections were weak and FWHM values were relatively high (0.33°) indicating partially amor-

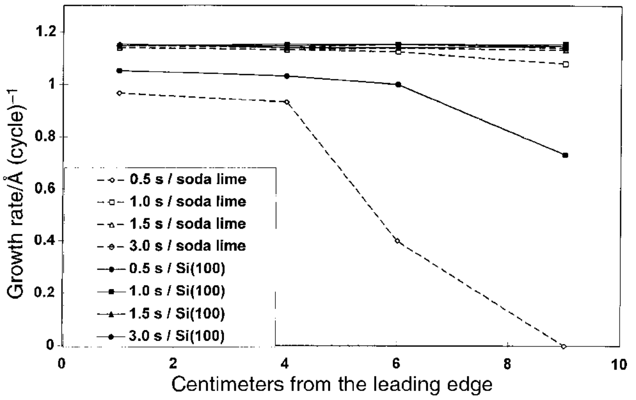


Fig. 3 Thickness profiles of MgO films as a function of $(C_5H_5)_2Mg$ pulse time. Precursor temperature was 50 °C, pulse length of H_2O was 0.5 s and purging times 0.8 s. Deposition temperature was 300 °C.

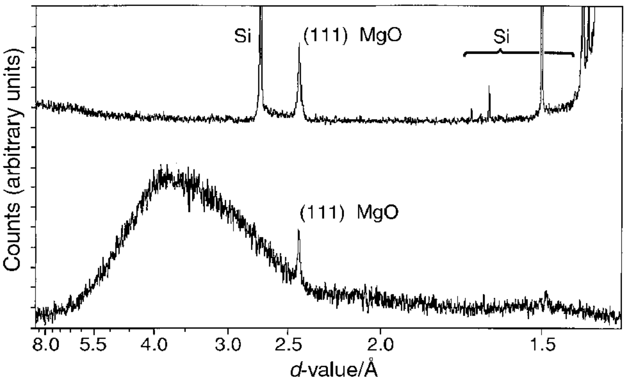


Fig. 4 X-Ray diffraction diagrams of 170 nm MgO films deposited at 300 °C onto Si(100) (top) and soda lime (bottom) substrates.

phous films. H_2O pulse times had no effect on the crystalline orientations or the intensities of the reflections. The texture is clearly different from films deposited from $Mg(thd)_2$, which resulted in predominantly (100) oriented films on similar substrates.[1] At much higher temperatures of 600–700 °C the MgO films deposited from $(C_5H_5)_2Mg$ also have the (111) orientation on Si(111) substrates.[9] Recently it has been observed in PE-CVD that a change in the orientation of MgO from (110) to (100) can be controlled by changing the O_2 flow rate, carrier gas flow rate and total pressure.[19]

Surface morphology of the deposited films was analyzed by AFM. At the first stage, the MgO films were deposited onto the Si(100) substrate at various temperatures with the thicknesses of 120–190 nm. Roughness of the MgO films showed an unusual behavior (Fig. 5a–d). Depositions carried at 200 °C or below resulted in smooth films with a roughness of ≈ 2 nm expressed as root mean square (rms). In this temperature range, the roughness of the films remained almost constant although the growth rate increased from 0.80 to 1.16 Å cycle^{-1}. After that, the rms values showed a clear increase in films deposited at 200–300 °C with a maximum value of ≈ 11 nm (Fig. 6), while the growth rate remained constant. As expected, depositions carried out below 200 °C produced amorphous MgO films. The sudden increase in roughness at 200 °C is probably caused by crystallization of the MgO film when the deposition temperature is increased. However, the drastic decrease in roughness when the growth temperature is raised above 300 °C may be due to increasing surface mobility or a change in the growth mechanism. When roughness values are compared to those of MgO films deposited by ALE from $Mg(thd)_2$ with equal thickness, it can be seen that rms values are 4–5 times higher.

Furthermore, to get some insight into thinner films of MgO, samples with a thicknesses of 3 and 10 nm were deposited at 300 °C onto Si(100) substrate. Roughness (rms) of these films were 0.19 and 0.20 nm, respectively. Films were uniform indicating controlled growth without an island-type mechanism (Fig. 5e and f).

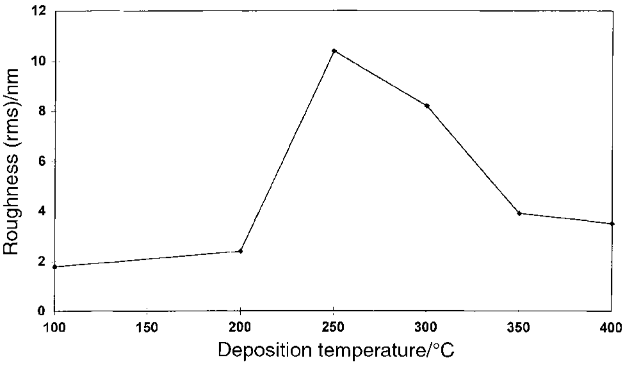


Fig. 6 Roughness (rms) of MgO films deposited onto Si(100) substrate as a function of deposition temperature.

The surface composition of MgO film deposited at 300 °C using optimised deposition parameters was also studied with XPS. In wide scan measurements, only magnesium, oxygen and carbon were detectable at the surface (Fig. 7). The carbon was mainly due to surface contamination caused by a short exposure to ambient air prior to the measurements. The carbon content of the surface (11–13 at%) agrees well with the typical surface contamination levels detected for oxides.

The chemical state of the elements detected was further examined using high resolution regional scans of C 1s, Mg 1p

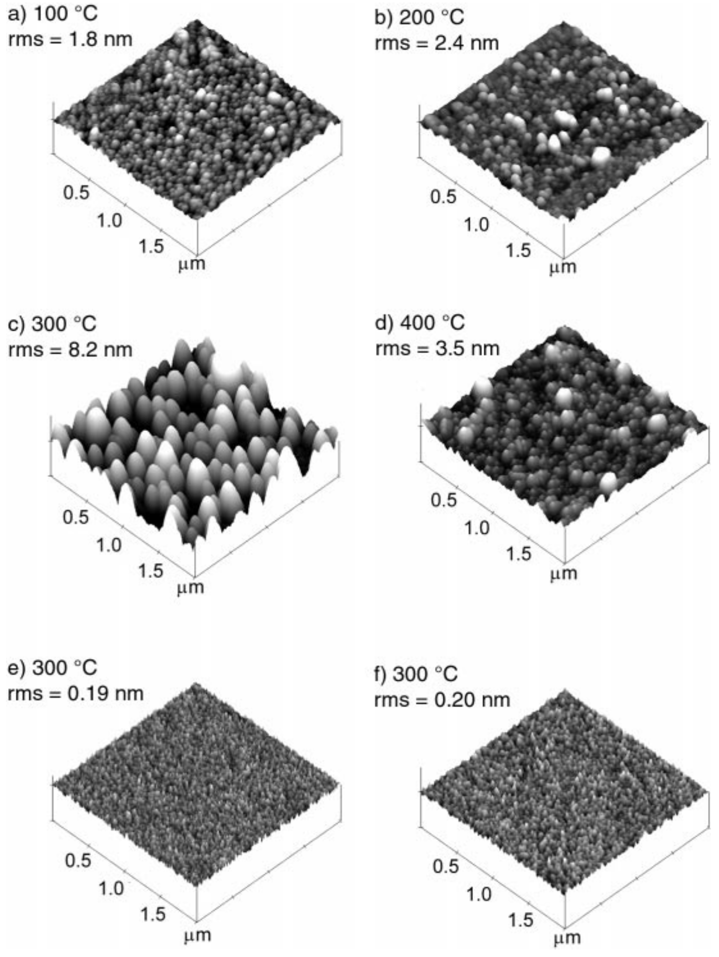


Fig. 5 AFM images taken from MgO films deposited at various temperatures onto Si(100) substrates. Thicknesses of measured samples were: (a) 190, (b) and (c) 170, (d) 120, (e) 3 and (f) 10 nm. The *z*-axis was 50 nm and 5 nm in images (a)–(d) and (e)–(f), respectively.

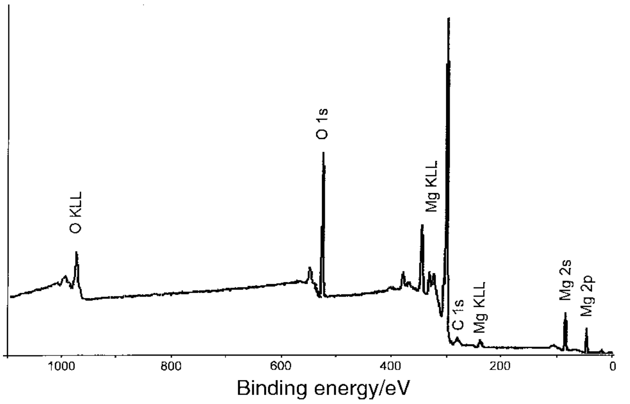


Fig. 7 XPS wide spectra of 170 nm MgO film deposited at 300 °C. The C 1s peak arises from surface contamination (air exposed samples).

and O 1s. The binding energies were calibrated using the C–C component of the C 1s spectra at 285 eV, although the calibration process was somewhat hindered by the strong, complex Mg KLL signal in the vicinity. Mg 2p yielded a sharp line at 49.5 eV, which is in good accordance with the tabulated binding energy for Mg in MgO.[20,21] In the O 1s signal two components were present. The major component at 529.9 eV fits well with tabulated values of O_{MgO}. Furthermore, the Mg : O_{MgO} atomic ratio was stoichiometric (1 : 1). The minor component of the O 1s signal at 532 eV was assigned to adsorbed OH groups. In some recent studies at HUT we have found that the intensity of this component increases with ageing of the highly hygroscopic magnesium oxide surface.[1]

Conclusions

The use of a cyclopentadienyl-type precursor for magnesium enables the growth of MgO thin films by ALE in a controlled manner at a relatively high rate. A surface-controlled growth was obtained in the temperature range of 200–300 °C with a deposition rate of 1.16 Å cycle^{-1} on soda lime and Si(100) substrates. The growth rate is approximately four to five times higher than that obtained under similar conditions from $Mg(thd)_2$ and ozone and ten times higher than with $Mg(thd)_2$ and hydrogen peroxide.[1,2] As expected, a linear dependence of the film thickness on the number of deposition cycles was observed indicating a typical ALE process.

Deposited films were polycrystalline with the (111) reflection dominating. The reflection was weak with a relatively high FWHM value indicating that the degree of crystallinity was low which is not unexpected due to the low deposition temperature. Impurity levels, especially those of carbon, were insignificant in the bulk of the film when MgO films were deposited in the ALE temperature window. 0.1 at% of carbon and 0.5 at% hydrogen were detected by ERDA in films deposited at 300 °C. However, hydrogen and also to some extent carbon content increased when the deposition temperature was lowered to below 200 °C. Deposited films were stoichiometric when deposition was carried out at 200–400 °C. According to AFM measurements the film roughness was greatly dependent on the deposition temperature. Deposition temperatures up to 200 °C resulted in quite smooth films with an rms roughness of 2 nm. Films deposited at 250–300 °C exhibited greater rms values of 8–12 nm although the thickness and growth rate remained the same. Above 300 °C the film roughness was again around 3 nm.

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