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Dr. L.C. Feldman  
Room 1E-351  
AT & T Bell Laboratories  
Murray Hill, New Jersey 07974  
USA

FAX: +1-908-582 4228

Professor Jun-ichi Nishizawa  
Tohoku University  
2-1-1 Katahira  
Aoba-ku, Sendai  
Japan 980

FAX: +81-22-262 3180

Professor W.F. van der Weg  
Department of Atomic and Interface Physics  
University of Utrecht  
P.O. Box 80.000, 3508 TA Utrecht  
The Netherlands

FAX: +31-30-543 165  
E-Mail: vdweg@fys.ruu.nl

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# Contents

Preface	vii
Conference organization	ix
Sponsors	x
 ATOMICALLY CONTROLLED FORMATION OF SURFACES AND INTERFACES	
Atomically abrupt semiconductor heterointerfaces: their role in advanced electronic and photonic devices and quantum phenomena F. Capasso	1
Bonding of carbon to nickel surfaces: effects of subsurface Na, H and C H. Yang, J.L. Whitten and R.J. Markunas	12
S <sub>B</sub> step growth mechanism on the reconstructed (001) surface: cluster migrations at the growing edge M. Hata, C. Ohara, S. Oikawa and M. Tsuda	21
First-order isothermal desorption kinetics of chlorine on SiH <sub>2</sub> Cl <sub>2</sub> -adsorbed Si(100) surface H. Sakamoto, Y. Takakuwa, T. Hori, T. Horie and N. Miyamoto	27
Precursor properties of calcium $\beta$ -diketonate in vapor phase atomic layer epitaxy J. Aarik, A. Aidla, A. Jaek, M. Leskelä and L. Niinistö	33
Nanofabrication of layered materials with the scanning tunneling microscope S. Kondo, M. Lutwyche and Y. Wada	39
Effects of oxygen on surface reconstruction of carbon J.L. Whitten, P. Cremaschi, R.E. Thomas, R.A. Rudder and R.J. Markunas	45
Atomic processes in the deposition and sintering of ultrafine metal particles on MgO(001) as investigated by molecular dynamics and computer graphics A. Miyamoto, R. Yamauchi and M. Kubo	51
Structure and electronic states of the Si(001)2 $\times$ 1/C surface by first-principles molecular dynamics calculations J. Yamauchi and M. Tsukada	58
RHEED reflex profile analysis and phase locked epitaxy of ZnSe on (001)-oriented GaAs J. Griesche, N. Hoffmann, M. Rabe and K. Jacobs	64
Growth of ZnS thin films by liquid-phase atomic layer epitaxy (LPALE) S. Lindroos, T. Kanninen and M. Leskelä	70
Ab initio models for ZnS surfaces: the influence of cluster size on surface properties. II. Three-dimensional models J. Muilu and T.A. Pakkanen	75
Desorption energies averaged over the desorption process by model calculations H. Siimon and T. Uustare	83
Electron-stimulated desorption of surface hydrogen on a Si(100) surface F. Hirose and H. Sakamoto	87
Epitaxial growth of metal-phthalocyanines on hydrogen-terminated Si(111) surfaces H. Tada, T. Kawaguchi and A. Koma	93
The effect of gaseous SiCl <sub>4</sub> on the ALE growth of CaS, SrS and SrS:Ce P. Soininen, L. Niinistö, E. Nykänen and M. Leskelä	99

Deposition rate of Ag on NaCl substrate in high temperature Ar gas of low concentration I. Ogura, Y. Jimba and S. Nagashima	106
Study of iron silicide formation on Si(111) by soft X-ray emission spectroscopy M. Kasaya, S. Yamauchi, M. Hirai, M. Kusaka, M. Iwami, H. Nakamura and H. Watabe	110
Analysis of the structure of two-dimensional layers of metal atoms adsorbed on the W(110) face based on electron work function experimental data L.A. Rudnitsky	115
An ab initio study of adsorbed carbon monoxide on a metal electrode by cluster model K. Watanabe, U. Nagashima and H. Hosoya	121

## CHARACTERIZATION OF SURFACES AND INTERFACES

STM of manipulated structures: characterization of metal oxide films Th. Bertrams, A. Brodde, H. Hannemann, C.A. Ventrice, Jr., G. Wilhelmi and H. Neddermeyer	125
Application of low-energy ion scattering to studies of growth H.H. Brongersma and J.-P. Jacobs	133
Solid phase epitaxy processes of amorphized silicon surfaces by Ar-ion bombardment observed "in situ" with ultra-high vacuum tunneling microscopy operated at high temperature T. Yao, K. Uesugi, M. Yoshimura, T. Sato, T. Sueyoshi and M. Iwatsuki	139
Multiphase surface morphologies of doped homoepitaxial diamond films H.G. Maguire, M. Kamo, H.P. Lang and H.-J. Güntherodt	144
Dissipation of contact-electrified charge on thin Si-oxide studied by atomic force microscopy S. Morita, Y. Fukano, T. Uchihashi, Y. Sugawara, Y. Yamanishi and T. Oasa	151
XPS-characterization of hydrogen-evolving platinum-coated p-silicon photoelectrodes G. Bilger, M. Specht, C.U. Maier, A. Eicke and M. Gillmann	157
Polarization-resolved photoluminescence of InAs/GaAs strained-layer structures on variously oriented substrates T. Shima, J.-S. Lee, K. Kudo, K. Tanaka, S. Niki, A. Yamada and Y. Makita	164
Surface structures of GaAs passivated by chalcogen atoms H. Shigekawa, H. Oigawa, K. Miyake, Y. Aiso, Y. Nannichi, Y. Saito, T. Hashizume and T. Sakurai	169
Characterization of interfaces between TiN or hard carbon coating and substrate by SIMS R. Zilliacus, J. Likonen, H. Ronkainen and J.-P. Hirvonen	175
In situ characterization of ALE growth by reagent pulse delay times in a flow-type reactor J. Aarik, A. Aidla and K. Kukli	180

## CONTROLLED ADSORPTION ON POROUS SURFACES

Atomic layer epitaxy (ALE) on porous substrates E.-L. Lakomaa	185
Adsorption of anionic and cationic polymers on porous and non-porous calcium carbonate surfaces R.B. Bjorklund, H. Arwin and L. Järnström	197
FT-IR and solid-state NMR investigation of surface hydroxyl groups on dealuminated ZSM-5 A. Maijanen, E.G. Derouane and J.B. Nagy	204
Studies of cellulose surfaces by titration and ESCA P. Stenius and J. Laine	213
Chemisorption of chromium acetylacetonate on porous high surface area silica S. Haukka, E.-L. Lakomaa and T. Suntola	220
Growth mechanism of long chain compounds on the surface of amorphous carbon film with normal molecular orientation K. Yase, M. Yamanaka, K. Mimura, K. Inaoka and K. Sato	228

## CONTROLLED FORMATION OF COMPLEX LATTICE STRUCTURES

Tailored heterointerface formation in InGaAs/InP superlattices by gas source migration-enhanced epitaxy T. Mozume, H. Kashima, K. Hosomi, K. Ogata, K. Suenaga and A. Nakano	233
Optical properties of atomically controlled InGaAs/InP quantum well structures H. Asahi, H. Ijuin, T. Kohara, K. Asami, H. Watanabe and S.-i. Gonda	242
Correlation between initial growth planarity and epilayer tilting in the vicinal GaAs/Si system F. Riesz, J. Varrio, A. Pesek and K. Lischka	248
Study of $(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta})_M/(\text{PrBa}_2\text{Cu}_{3-x}\text{Ga}_x\text{O}_{7-\delta})_N$ superlattices grown by pulsed-laser deposition: a comparison between <i>a</i> - and <i>c</i> -axis-oriented structures J.P. Contour, C. Sant, D. Ravelosona, C. Dolin, J. Perrière, L. Ranno, P. Auvray and J. Caulet	252
Staircase-like structures in in situ optical reflectance measurement as an evidence for two-dimensional crystal growth in layer-by-layer chemical vapor deposition of $\text{YBa}_2\text{Cu}_3\text{O}_x$ S. Oda, K. Sakai and H. Zama	259
X-ray crystal truncation rod scattering from MBE grown $(\text{CaF}_2\text{-SrF}_2)/\text{Si}(111)$ superlattices J. Harada, Y. Itoh, T. Shimura, I. Takahashi, J.C. Alvarez and N.S. Sokolov	263
Controlled formation and characteristics of interfaces in GaAs/AlGaAs single quantum wells X. Wang, H. Zheng, T. Yu and R. Laiho	269
Thermal processing of strained-layer InGaAs/GaAs quantum well interface G. Zhang and M. Pessa	274
Growth control of InAs thin layers on GaAs substrates with several orientations J.-S. Lee, T. Shima, K. Kudo, K. Tanaka, S. Niki, A. Yamada and Y. Makita	279
Adsorption and decomposition of triethylindium on GaP(001) studied by X-ray and ultra-violet photoelectron spectroscopy Y. Fukuda, Y. Suzuki, J. Murata and N. Sanada	285
Fabrication and optical study of zinc-blende MnTe epitaxial films grown on surface-controlled GaAs H. Akinaga and K. Ando	292
Heterointerfaces of CdTe/ $\alpha$ -Sn/InSb structure grown by molecular beam epitaxy A. Sasaki, T. Suzuki, M. Kimata, M. Yano and K. Kawamura	298
Determination of the conduction band discontinuity of a semiconductor n-N heterojunction W.C. Kok	303

## MAGNETO-OPTICAL AND DIELECTRIC FILMS

Controlled formation of oxide materials by laser molecular beam epitaxy H. Koinuma and M. Yoshimoto	308
Magnetic thin films and multilayers E. Bruno and B.L. Gyorffy	320
RHEED intensity oscillation during synthesis of ceramic superlattice thin films: migration-assisted epitaxial growth of magnesium oxide/titanium oxide superlattice F. Imai, K. Kunimori and H. Nozoye	326
Zirconium dioxide thin films deposited by ALE using zirconium tetrachloride as precursor M. Ritala and M. Leskelä	333
In situ oxidation of ultrathin layers of Ge on Si(001): evidence for bonding partner exchange K. Prabhakaran, T. Nishioka, Y. Kobayashi and T. Ogino	341
Author index	348
Subject index	352

# Zirconium dioxide thin films deposited by ALE using zirconium tetrachloride as precursor

Mikko Ritala \*, Markku Leskelä

*Department of Chemistry, University of Helsinki, P.O. Box 6, SF-00014 Helsinki, Finland*

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## Abstract

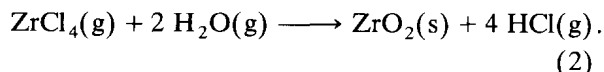
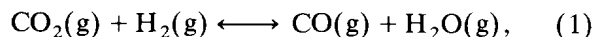
ZrO<sub>2</sub> thin films were grown by the atomic layer epitaxy (ALE) technique using ZrCl<sub>4</sub> and water as reactants. At 500°C amorphous films with good thickness uniformities were deposited onto soda lime glass substrates. However, rather long pulse and purge times were needed to realize the self-controlled growth. Films were characterized by means of spectrophotometry, RBS, NRA, SEM and AFM.

## 1. Introduction

ZrO<sub>2</sub> is characterized by extreme thermal, chemical and mechanical stability which together with its optical and electrical properties gives rise to a wide range of technical applications for ZrO<sub>2</sub> thin films and coatings, especially in optics [1], electronics [2,3] and protective applications [4]. When mixed with other oxides, like Y<sub>2</sub>O<sub>3</sub>, MgO, CaO or CeO<sub>2</sub>, ZrO<sub>2</sub> becomes stabilized against phase transformations which facilitates its use in thermal barrier coatings [5,6]. Moreover, the oxygen ion conducting property of ZrO<sub>2</sub> based oxide mixtures [7,8] gives rise to further applications for these films and coatings, e.g., in gas sensors [9] and fuel cells [10].

Besides numerous physical vapor deposition techniques, like plasma spraying [5] and ion-assisted deposition [11], also sol-gel method [4,12]

and chemical vapor deposition (CVD) have been used to deposit ZrO<sub>2</sub> films. The most typical zirconium compounds exploited in CVD are ZrCl<sub>4</sub> [2,13–17],  $\beta$ -diketonates [18–22] and alkoxides [1,23,24]. However, the use of ZrCl<sub>4</sub>, the most readily available volatile zirconium precursor, is complicated due to its facile hydrolysis and oxidation resulting in premature gas-phase reactions and powder formation [13,16,17,21]. This problem is normally circumvented by generating water in situ from a mixture of CO<sub>2</sub> and H<sub>2</sub> near the heated substrate surface (Eq. (1)) [2,13–16]. The water formed reacts immediately with ZrCl<sub>4</sub> (Eq. (2)). As a consequence of the strong temperature dependence of the water formation the film growth is controlled conveniently by means of the substrate temperature.



However, this process suffers from the high tem-

\* Corresponding author.



perature needed for the water formation. Even though the film growth does take place at 600°C [16] substrate temperatures higher than 800°C are generally exploited in order to realize a reasonable deposition rate. Consequently, the choice of the substrate material is essentially limited. Moreover, it has been observed that some carbon is incorporated into the films [14].

The characteristic feature of the atomic layer epitaxy (ALE) technique is the alternate dosing of the reactants which avoids the gas-phase reactions. We have demonstrated earlier that TiO<sub>2</sub> films with good thickness uniformities can be deposited by ALE using TiCl<sub>4</sub> and water as reactants [25]. The general similarity of this process to the ZrCl<sub>4</sub>/water system inspired us to the present work where the possibilities of ALE to deposit ZrO<sub>2</sub> films onto soda lime glass substrates have been studied.

## 2. Experimental

Film deposition was carried out with a commercial flow type F-120 ALE-reactor (Microchemistry Ltd., Finland) [26] using nitrogen as a

carrier and purging gas. Total pressure of the reactor was in the order of 10 mbar. ZrCl<sub>4</sub> (99.9% purity; Aldrich) was evaporated from an open boat at 165°C. An external water reservoir held at 20°C was connected to the cold end of the reactor through a capillary and a needle valve. Water was introduced into the reactor by means of its own pressure without any bubbling systems. The pulsing of the reactants was realized by means of computer-controlled solenoid valves. The films were deposited onto 5 × 5 cm<sup>2</sup> soda lime glass substrates at 500°C.

Film thicknesses were determined by fitting transmittance spectra using the method developed and described by Ylilammi and Ranta-aho [27]. Transmittance spectra covering wavelengths of 380–1100 nm were measured with a Hitachi U-2000 spectrophotometer equipped with a special sample holder. Stoichiometry and possible chlorine residues of the films were analyzed by means of Rutherford backscattering spectrometry (RBS) of 2.0-MeV <sup>4</sup>He<sup>+</sup> ions from the 2.5-MV Van de Graaff accelerator of the Accelerator Laboratory, University of Helsinki [28]. RBS also provided comparative thickness values. Hydrogen contents were determined by the nuclear reaction

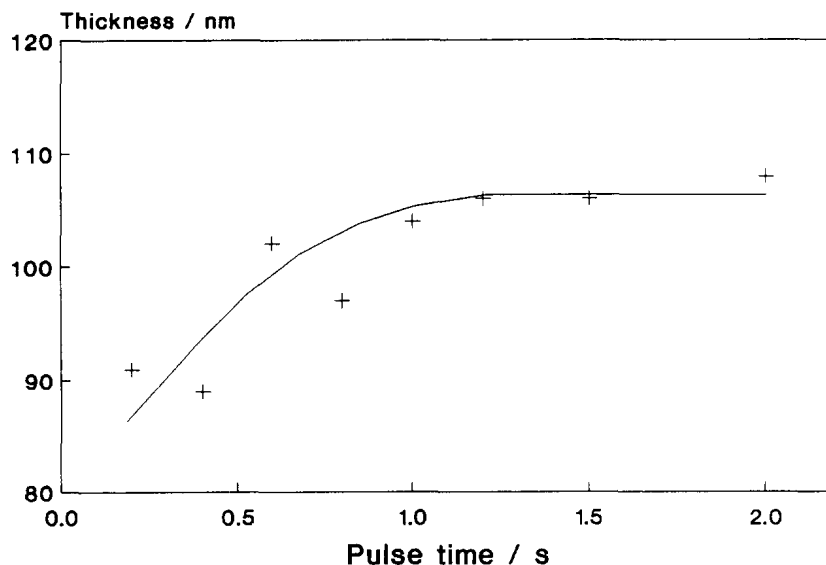


Fig. 1. The dependence of film thicknesses on the reactant pulse lengths for films deposited at 500°C using 2000 reaction cycles. The purge times used were 3.0 s except for 2.0 s pulse times where 4.0 s purging sequences were employed.

analysis (NRA) technique using a  $^{15}\text{N}^{2+}$  beam from the 5-MV tandem accelerator EGP-10-II of the Accelerator Laboratory to excite the 6.385 MeV resonance of the  $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$  reaction [29]. Crystallinity of the films was examined by XRD measurements using a Philips MPD 1880 powder X-ray diffractometer and  $\text{Cu K}\alpha$  radiation. A JEOL JSEM-820 scanning electron microscope (SEM) and a Nanoscope II atomic force microscope (AFM) were exploited for the morphological characterization.

### 3. Results and discussion

#### 3.1. Film growth

The dependence of film thicknesses on pulse durations is shown in Fig. 1 for films grown at 500°C using 2000 reaction cycles. A saturated film thickness of 105 nm was achieved with pulse times exceeding 1.0 s. Even with the shortest pulse times used the film thicknesses were already in the order of 90 nm suggesting that the saturation is controlled mainly by surface processes instead of mass transfer. When the pulse time of one reactant was fixed to 1.0 s, i.e., to the value needed for saturation, and the length of the other pulse was varied independently, it was observed that the  $\text{ZrCl}_4$  pulse was the critical one in respect of the thickness saturation. The water pulse could be shortened to 0.2 s with no effect on film thicknesses, whereas short  $\text{ZrCl}_4$  pulses resulted in thicknesses comparable to those obtained having both pulses short (Fig. 1). Thus, the surface processes following the adsorption of  $\text{ZrCl}_4$  were interpreted to be responsible for the long pulse times needed.

The growth rate corresponding to the saturated thickness value is 0.53 Å/cycle showing that only a submonolayer of  $\text{ZrO}_2$  was deposited during one cycle. The apparent origin of growth rates less than a monolayer per cycle met in various ALE processes is the bulkiness of the precursor molecules [30].

The data shown in Fig. 1 was obtained using 3.0 s purge durations except for the 2.0 s pulses where longer purging (4.0 s) was needed to

achieve good thickness uniformity. The effect of the purge time was studied in detail with 1.5 s pulse durations (Fig. 2). The thicknesses shown were measured at the center of the substrates. Thus, even though 2.0 s purging was sufficient to achieve a constant thickness value at this particular point longer purge sequences (3.0 s) were needed to obtain the overall thickness uniformity. The insufficient purging resulted in films with thicknesses increasing towards the end of the substrate. As the purge time was increased the stabilized thickness values were obtained initially at the leading edge of the substrate while the area of insufficient purging contracted towards the end of the substrate (Fig. 3). The films deposited with insufficient purging were profiled not only in the flow direction but also perpendicular to it, being thickest at the middle.

The independent variation of the purge durations after the two reactant pulses showed that the purge sequence following the water pulse was the critical one. Even with short water pulses long purge sequences were needed. On the other hand, the purge period after the  $\text{ZrCl}_4$  pulse could be shortened to one second without any effect on the thickness uniformity.

Perhaps the most crucial question in respect of both the growth mechanism and, consequently, the origin of the long purge time needed is whether the film surface remains hydroxyl-terminated or not after the water pulse. Unfortunately, the compact design of our reactor chamber makes any kind of in situ characterization technique needed to answer this question extremely difficult to realize. Some guidance to this problem is obtained from the IR studies of Agron et al. [31] which have shown that even after extensive outgassing in vacuum at 500°C considerable amounts of hydroxyl groups bonded to more than a single cation are retained on the surface of  $\text{ZrO}_2$  powder. Nevertheless, since the chemical environment on the growing film surface is likely to differ essentially from that on the surface of powder pressed in dies, these results can be regarded as only tentative. Therefore, both possibilities, i.e., hydroxylated and dehydroxylated surfaces, will be considered.

If the surface did remain hydroxyl-terminated

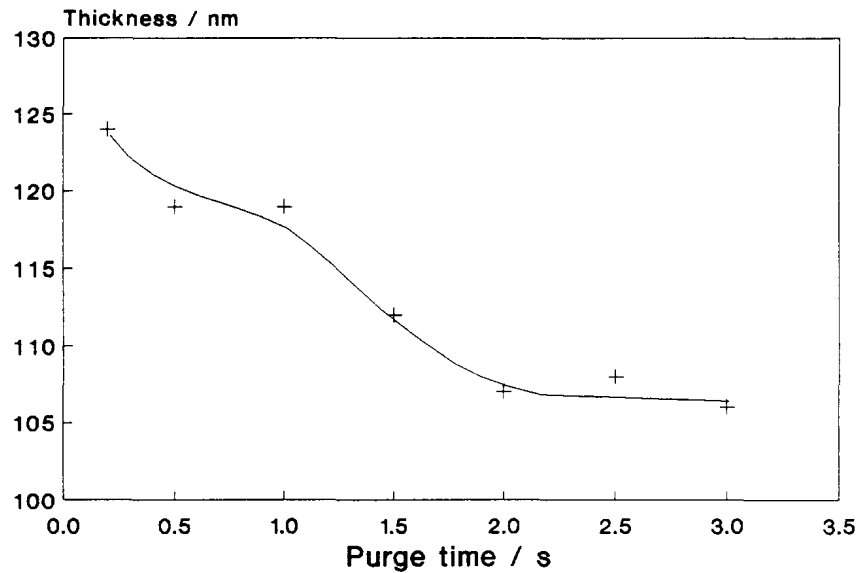


Fig. 2. The film thicknesses as a function of the purge durations. The data were measured at the center of the films grown by 2000 cycles at 500°C using 1.5 s reactant pulses.

the film growth would be expected to involve irreversible reactions of  $\text{ZrCl}_4$  with surface hydroxyls resulting in a chlorine-terminated surface and liberation of HCl. The subsequent water pulse would convert the surface back into a hy-

droxyl-terminated one. In this case the slow processes which need the long purge time could be either the condensation of unstable hydroxyl groups or the desorption of molecular water. Holmes et al. [32] have observed that large quan-

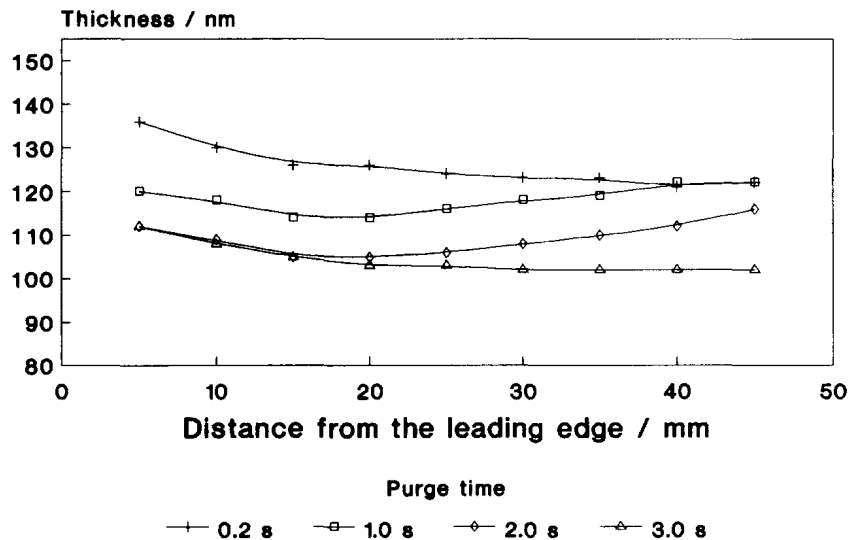


Fig. 3. The thickness profiles along the flow direction for films deposited using various purge times.

ties of water are irreversibly adsorbed on  $\text{ZrO}_2$  surfaces at ambient temperatures and attributed this to the formation of a hydrogen-bonded network of water on the top of the surface hydroxyl groups. Even though this effect is considerably reduced at elevated temperatures, even at  $400^\circ\text{C}$  three adsorption–desorption cycles were needed until a reversible equilibrium was obtained on the outgassed  $\text{ZrO}_2$  surface [32]. Thus, it seems feasible that even at  $500^\circ\text{C}$  the desorption of molecular water from the hydroxyl-terminated surface could be slow enough to account for the long purge periods needed.

On the other hand, if the film surface were completely dehydroxylated after the water pulse the mechanism in the film deposition would be the chemisorption of  $\text{ZrCl}_4$  followed by its hydrolysis. Since the strong adsorption of molecular water on  $\text{ZrO}_2$  was attributed to hydrogen bonding to the hydroxyl groups it is likely to be insignificant on a dehydroxylated surface and, thus, in this case the long purge time could be related to dehydroxylation processes.

The thickness profile at the leading edge of the substrate observed in all films (Fig. 3) is characteristic of the reactor used [25]. It is caused by the desorption of one reactant from walls

upstream the substrate during a pulse sequence of the other reactant, resulting in a CVD-like growth. Due to the facile reaction between  $\text{ZrCl}_4$  and water the desorbed species are exhausted from the vapor phase almost immediately after the crossing point of the reactant flow routes. However, since in our reactor this point is only about 1 cm ahead of the substrate, the tail of the CVD growth region overlaps with the leading edge of the substrate.

One of the attractive features of the ALE technique is that the film thickness is controlled simply by the number of reaction cycles used. In the present study the ideal linear relationship was confirmed (Fig. 4).

A slight thickness difference ( $<5\%$ ) was observed between films deposited using two  $\text{ZrCl}_4$  grades, one freshly opened and the other one being used for a couple of months. The most likely origin for this difference is a partial decomposition of  $\text{ZrCl}_4$  when exposed repeatedly to air as the reactor was loaded.

### 3.2. Film properties

The adhesion of the films was studied by the adhesive tape test. No adhesion failures were

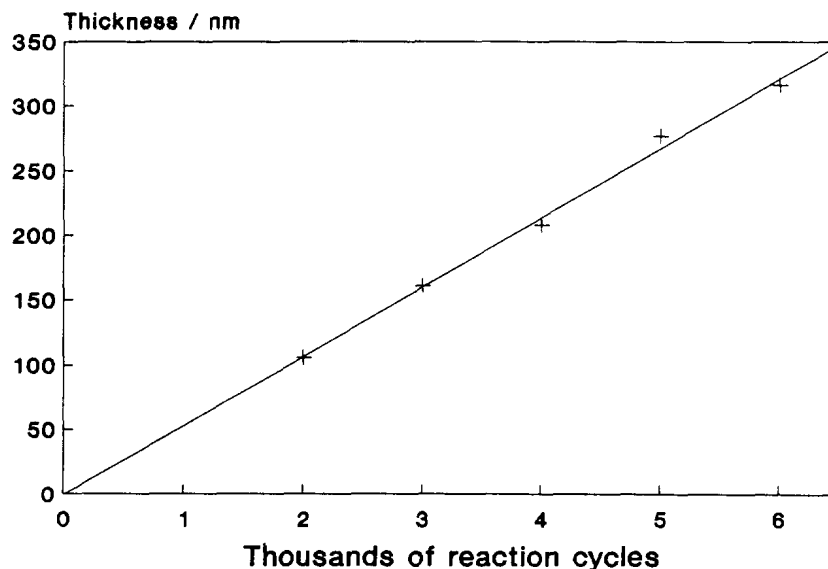


Fig. 4. Film thicknesses versus the number of reaction cycles used.

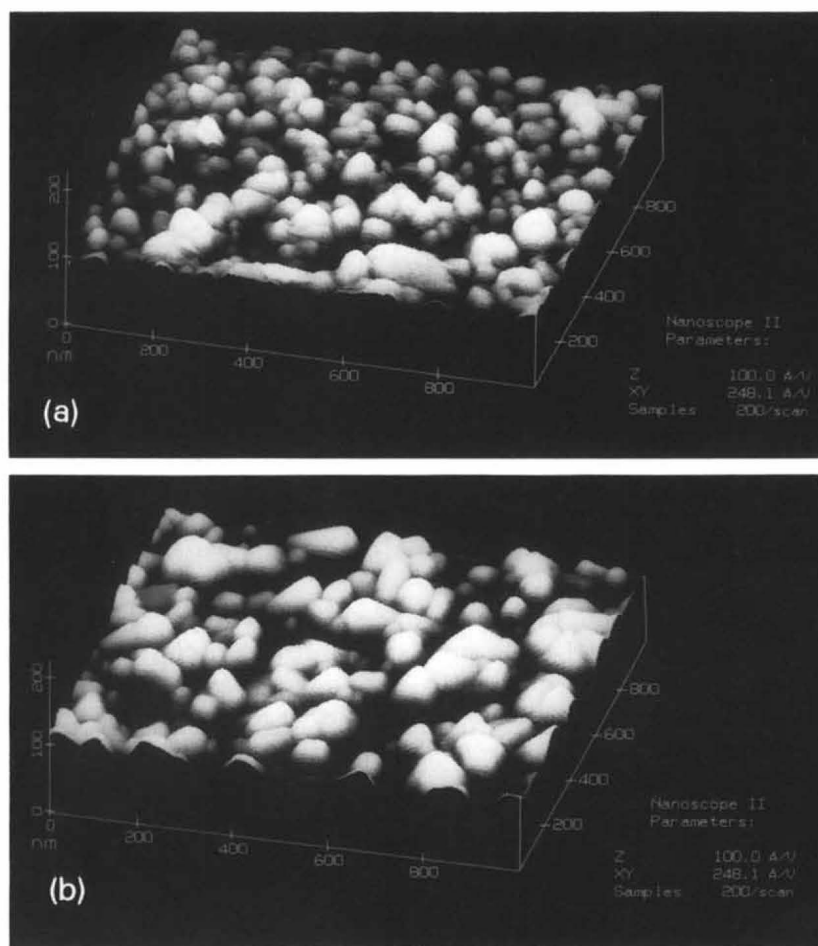


Fig. 5. AFM-images of films deposited using 2000 (a) and 4000 (b) reaction cycles.

observed in these tests. Cross-sectional SEM micrographs showed that films consisted of densely packed granules extending through the whole

film. The lateral diameter of these granules was in the order of 100–200 nm. It was also observed that the film surface was essentially rougher than

Table 1

Total range and standard deviations of  $z$ -values obtained from  $500 \times 500 \text{ nm}^2$  AFM scan images of bare soda lime glass substrate and of films deposited using 2000 and 4000 reaction cycles; the nominal thicknesses were obtained from the transmittance measurements

Number of deposition cycles	Nominal film thickness (nm)	$z$ -range (nm)	Standard deviation of $z$ (nm)	Standard deviation of $z$ /number of deposition cycles (nm)
0	0	5.3	0.5	~
2000	105	72	10.0	$5.0 \times 10^{-3}$
4000	210	83	12.6	$3.2 \times 10^{-3}$

the film–substrate interface, revealing that considerable roughening had occurred during the film growth.

The surface morphology was studied in more detail by means of AFM. In spite of their good thickness uniformity on a macroscopic scale, the films showed significant roughening on a microscopic scale (Fig. 5). Numerical estimations about the surface roughnesses were obtained from the standard deviations and the total ranges of the  $z$ -values obtained from  $500 \times 500 \text{ nm}^2$  scan areas (Table 1). The standard deviations divided by the number of deposition cycles used show that roughening has occurred more heavily during the first 2000 cycles as compared to the subsequent 2000 cycles. All these observations are parallel with our previous results [33] about the morphological development of ALE-deposited  $\text{TiO}_2$  films. According to that study, roughening has its origin in agglomeration which was most intense during the very first deposition cycles. Obviously, the agglomeration is driven by the film–substrate interface energy. On the other hand, there is no unambiguous explanation for the agglomeration mechanism, but surface migration of hydroxyl groups or gas-phase migration of volatile intermediates seem to be the most feasible ones [33].

XRD measurements revealed that the films were nearly amorphous. Only some weak reflections attributed either to monoclinic or tetragonal  $\text{ZrO}_2$  were observed. Obviously, elevation of the deposition temperature would enhance crystallization but with soda lime glass substrates  $500^\circ\text{C}$  is close to the upper limit. On the other hand, our studies concerning ALE deposition of  $\text{TiO}_2$  have shown that also the substrate materials and the precursor compounds have a strong effect on the film crystallinity [25,34]. Therefore, it seems possible that the crystallinity of the ALE-deposited  $\text{ZrO}_2$  films would be improved as well if crystalline substrates and/or different precursors were used.

RBS measurements confirmed that films were stoichiometric  $\text{ZrO}_2$ . No chlorine was observed by RBS showing that the possible chlorine contamination was below 0.5 at%. Conversion of the mass densities obtained from RBS to geometrical thicknesses, using the density of monoclinic  $\text{ZrO}_2$ ,

gave values comparable to those obtained by transmittance measurements. The close agreement of the two methods can be regarded as an indication of high film densities. However, the fact that the thicknesses obtained by RBS were the smaller ones may be indicative of slightly reduced film densities, caused most probably by the surface roughness.

Hydrogen contents of the films were determined by nuclear reaction analysis. Below the outermost surface layers the hydrogen content was less than 0.4 at%. Based on the facile adsorption of water on oxide surfaces, the hydrogen profiles can be exploited when assessing densities of oxide films [35,36]. For a comparison, Martin et al. [11] have reported that electron-beam-evaporated  $\text{ZrO}_2$  film contains 10 at% hydrogen. Even though significant film densification was achieved with Ar ion assistance the hydrogen content was still in the order of 1 at% [11]. Thus, the observed low hydrogen contents give further evidence about the high densities of ALE-deposited  $\text{ZrO}_2$  films.

The films were highly transparent; no light absorption or scattering was observed in transmittance measurements. Refractive indices evaluated from the transmittance spectra were in the order of 2.2 which is comparable to the highest ones observed in CVD-deposited films [2,19]. The refractive indices along different crystal axes of monoclinic  $\text{ZrO}_2$  crystals are 2.13, 2.19 and 2.20 [37]. Thus, the refractive indices are in good accordance with the earlier observations about high film densities.

#### 4. Conclusions

$\text{ZrO}_2$  thin films were deposited by ALE. The reactants used were  $\text{ZrCl}_4$  and water, which is known to be a difficult combination in CVD processes because of premature gas-phase reactions. The sequential dosing of the reactants in ALE eliminated this problem and since no in situ water generation was needed the deposition temperature ( $500^\circ\text{C}$ ) used was considerably lower than those needed in CVD processes employing  $\text{ZrCl}_4$ . The films deposited onto glass substrates

were highly transparent and had good thickness uniformities. According to the XRD measurements the films were nearly amorphous. The high refractive indices, the low hydrogen contents in the bulks of the films, as well as the close agreement between the thickness values obtained from RBS and transmittance measurements proved that the films had a high density. However, SEM and AFM showed that considerable roughening had occurred during the film growth.

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