

# MATERIALS SCIENCE & ENGINEERING

## **B** **Solid-State Materials for Advanced Technology**

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## Contents

<b>Preface</b> .....	vii
<b>Plenary Lectures</b>	
Crystal technology for future applications of high temperature superconductors S. Tanaka (Tokyo, Japan) .....	1
Effect of high energy electron irradiation on YBCO and application to Josephson junction fabrication W.Y. Liang, J. Yuan, Y. Yan, A.J. Pauza (Cambridge, UK) .....	5
New theory of superconducting copper oxides—from electronic structure to the d-wave pairing mechanism H. Kamimura, S. Matsuno, Y. Suwa (Tokyo, Japan), H. Ushio (Hachioji, Japan) .....	10
Phase formations and electrical properties of doped-PZT/PbTiO <sub>3</sub> films deposited by reactive sputtering using multi-targets G.-P. Choi, J.-H. Ahn, W.-J. Lee, T.-H. Sung, H.-G. Kim (Taejon, South Korea) .....	16
Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications L. Niinistö (Espoo, Finland), M. Ritala, M. Leskelä (Helsinki, Finland) .....	23
Evolution of oxide electronics: examples from HTS and CMR T. Venkatesan, R.P. Sharma (MD, USA) .....	30
<b>Physics/Chemistry</b>	
Electron tunneling through ultrathin SiO <sub>2</sub> M. Hirose (Higashi-Hiroshima, Japan) .....	35
Approach to novel crystalline and amorphous oxide materials for optoelectronics by ion implantation H. Hosono, H. Kawazoe (Yokohama, Japan) .....	39
Molecular dynamics simulation of oxygen ion diffusion in Ba <sub>2</sub> In <sub>2</sub> O <sub>5</sub> M. Kanzaki, A. Yamaji (Tokyo, Japan) .....	46
Cooperative interaction of oxygen octahedra for dielectric properties in the perovskite-related layered compounds Sr <sub>n+1</sub> Ti <sub>n</sub> O <sub>3n+1</sub> , Ca <sub>n+1</sub> Ti <sub>n</sub> O <sub>3n+1</sub> and Sr <sub>n+1</sub> (Ti <sub>0.5</sub> Sn <sub>0.5</sub> ) <sub>n</sub> O <sub>3n+1</sub> (n = 1, 2, 3 and ∞) J.-H. Sohn, Y. Inaguma, M. Itoh, T. Nakamura (Yokohama, Japan) .....	50
Valency pair and properties of 1:1 ordered perovskite-type compounds Sr <sub>2</sub> MMoO <sub>6</sub> (M = Mn, Fe, Co) M. Itoh, I. Ohta, Y. Inaguma (Yokohama, Japan) .....	55
High-pressure synthesis and thermal decomposition of LaCuO <sub>3</sub> M. Karppinen, H. Yamauchi, T. Ito, H. Suematsu (Yokohama, Japan), O. Fukunaga (Tokyo, Japan) .....	59
Local structure around oxygen atoms in CaMgSi <sub>2</sub> O <sub>6</sub> glass by O K-edge EXELFS Y. Tabira (Yokohama, Japan) .....	63
Structural and optical characterization of Pb <sub>x</sub> Ti <sub>1-x</sub> O <sub>2</sub> film prepared by sol-gel method M. Mosaddeq-ur-Rahman, T. Miki, K.M. Krishna, T. Soga, K. Igarashi, S. Tanemura, M. Umeno (Nagoya, Japan) .....	67
Photoacoustic spectroscopy of Cr <sup>3+</sup> in Ceramic Al <sub>2</sub> O <sub>3</sub> T. Toyoda, T. Obikawa (Tokyo, Japan) .....	72
<b>Superconductivity and Oxide Superconductors</b>	
Anisotropic superconductivity and oxide electronics I. Iguchi, K. Lee (Tokyo, Japan) .....	76
Microstructural study on 90° basal-plane-faced tilt boundaries showing d-wave pairing characteristics J.G. Wen, Y. Ishimaru, K. Hayashi, Y. Enomoto, N. Koshizuka (Tokyo, Japan) .....	82
Preparation of thin films of YBa <sub>2</sub> Cu <sub>3</sub> O <sub>x</sub> with a smooth surface by atomic layer MOCVD S. Yamamoto, A. Kawaguchi, S. Oda (Tokyo, Japan) .....	87
Direct evidence for the STM observation of CuO <sub>2</sub> plane in Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8+x</sub> and possibility of new tunnel transistor operation M. Nishiyama, K. Ogawa (Yokohama, Japan), T. Mochiku, K. Kadowaki (Ibaraki, Japan) .....	93
Fabrication and characterization for single crystal substrates of YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-δ</sub> and related materials H. Zama, F. Wang, S. Koyama, X. Yao, M. Tagami, Y. Shiohara, T. Morishita (Tokyo, Japan) .....	98



Photoacoustic spectra of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ ( $x = 0.0, 0.65, \text{ and } 1.0$ )	
T. Toyoda, I. Shiozaki (Tokyo, Japan) . . . . .	102
Change in phonon Raman spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+d}$ induced by hole filling and implications for phonon assignments	
M. Osada, M. Kakihana (Yokohama, Japan), M. Käll (Roskilde, Denmark), L. Börjesson (Goteborg, Sweden), M. Yashima, M. Yoshimura (Yokohama, Japan) . . . . .	107
Microstructure of Ag-sheathed $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ tape	
H. Suematsu, H. Yamauchi (Yokohama, Japan), T. Yano (Meguroku, Japan), H. Ii, Y. Tanaka (Tochigi, Japan) . . . . .	111
<b>Oxide Thin Films</b>	
Processing and ultraviolet patterning of $\text{LiNbO}_3$ epitaxial films from metallorganic precursors	
S.-i. Hirano, T. Yogo, K.-i. Kikuta, W. Sakamoto, Y. Takeichi (Nagoya, Japan) . . . . .	117
Harmonic integration of functional metal oxide artificial lattices	
T. Kawai, M. Kanai, H. Tabata (Osaka, Japan) . . . . .	123
Thin film growth of $\text{SrBiTiO}$ system by PLD method and optical characterization	
M. Tachiki, K. Yamamuro, T. Kobayashi (Osaka, Japan) . . . . .	131
Molecular layer-by-layer growth of $\text{SrTiO}_3$ and $\text{BaTiO}_3$ films by laser molecular beam epitaxy	
T. Maeda, G.H. Lee, T. Ohnishi, M. Kawasaki, M. Yoshimoto, H. Koinuma (Yokohama, Japan) . . . . .	134
Preparation and characterization of highly $c$ -axis-oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films	
M. Yamaguchi, K. Kawanabe, T. Nagatomo, O. Omoto (Tokyo, Japan) . . . . .	138
Structure and electric properties of $\text{TiO}_2$ films prepared by cold plasma torch under atmospheric pressure	
H. Ha (Yokohama, Japan), B.K. Moon, T. Horiuchi, T. Inushima (Kanagawa, Japan), H. Ishiwara, H. Koinuma (Yokohama, Japan) . . . . .	143
$\text{BaTiO}_3/\text{SrTiO}_3$ thin films grown by an MBE method using oxygen radicals	
H. Shigetani, M. Fujimoto (Gunma, Japan), W. Sugimura (Tokyo, Japan), Y. Matsui, J. Tanaka (Ibaraki, Japan) . . . . .	148
Advanced processing and characterization of $\text{SrTiO}_3$ single crystals and bicrystals for high- $T_c$ superconducting film substrate	
K. Takahashi, A. Ohtomo, M. Kawasaki, H. Koinuma (Yokohama, Japan) . . . . .	152
Formation of high-dielectric oxide films on $\text{SrVO}_{3-x}\text{Si}$ substrates	
B.K. Moon, E. Tokumitsu, H. Ishiwara (Yokohama, Japan) . . . . .	157
Ambient-pressure influence on droplet formation and thickness distribution in pulsed laser ablation	
A. Masuda, K. Matsuda, S. Usui, Y. Yonezawa, T. Minamikawa, A. Morimoto, T. Shimizu (Kanazawa, Japan) . . . . .	161
<b>Device Applications</b>	
A proposal of epitaxial oxide thin film structures for future oxide electronics	
M. Suzuki, T. Ami (Yokohama, Japan) . . . . .	166
$\text{Pt/SrBi}_4\text{Ti}_4\text{O}_{15}/\text{Si}$ -MOS system: preliminary study employing an inverted MOS configuration	
K. Yamamuro, M. Tachiki, T. Kobayashi (Osaka, Japan) . . . . .	174
Role of hetero-junctions in oxide semiconductor gas sensors	
N. Yamazoe, J. Tamaki, N. Miura (Fukuoka, Japan) . . . . .	178
Characterization of crystallographic defects in thermally oxidized SIMOX materials	
L.F. Giles, Y. Kunii (Kanagawa, Japan) . . . . .	182
Preparation of zinc oxide varistor by a wet chemical method	
M. Takehana, T. Nishino, K. Sugawara, T. Sugawara (Akita Pref., Japan) . . . . .	186
<i>Author index</i> . . . . .	191
<i>Subject index</i> . . . . .	193
<i>Appendix</i> . . . . .	197

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# Synthesis of oxide thin films and overlayers by atomic layer epitaxy for advanced applications

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## Abstract

Atomic layer epitaxy (ALE) as a self-limiting thin film growth process results in several practical advantages including accurate and simple thickness control, large area and large batch capability, good conformality and reproducibility, straightforward doping and scale-up, possibility to produce sharp and tailored interfaces as well as capability to prepare multilayer structures in a continuous process. In this paper the use of ALE in deposition of numerous conducting and insulating oxide thin films will be reviewed. The versatile ALE chemistry allows the use of different types of metal-containing precursors from simple inorganic compounds to organometallics. Commonly used oxygen sources include water, oxygen, ozone, hydrogen peroxide and alcohols. The recent advances in oxide ALE processes, i.e. deposition of ternary and quaternary oxides, controlled doping of transparent conductors, preparation of multilayer structures as well as conformal coating of porous silicon will also be discussed in respect to their practical applications.

*Keywords:* Atomic layer epitaxy; Organometallics; Oxide thin films

## 1. Introduction

Stoichiometric oxide materials are characterized by high thermal and chemical stability and resistance to oxidation [1]. These features make the oxides fascinating materials to be used also in thin film application. Most oxides have ionic type bonding and lattice which usually results in optical transparency, high electrical resistivity, diamagnetism and low thermal conductivity. Electrically oxides may also be conducting, semiconducting or even superconducting which further expands their potential range of use in electronic and optoelectronic applications [2].

Usually the oxide thin films employed in applications are amorphous or polycrystalline. There has not been strong research nor a need for epitaxial oxide films until the interest devoted to oxide superconductors and ferroelectric materials [3]. The layer-type structure and the complicated stoichiometry of the superconducting oxides require atomic level control of the growing thin

films [4]. Therefore pulsed systems, viz. MBE and pulsed-MOCVD, have been extensively employed in the deposition of binary and ternary oxides, quaternary superconductors and the buffer layer oxide thin films [5–10].

Our interest to oxide thin films stems from their use in large area applications like electroluminescence displays and solar cells. There the desirable properties of the deposition process and the resulting films include homogeneous coating of large areas, pinhole-freeness, possibility to deposit different films in one pump-down and controlled doping of the films. The atomic layer epitaxy (ALE) process appears to fulfill these requirements [11–13].

## 2. Atomic layer epitaxy

The ALE method invented in the early 1970s by Suntola et al. [14] has received increasing interest because of its unique digital growth process [11,15]. ALE-growth proceeds by exposing the substrate surface alternately to the precursors and accordingly the depo-

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Table 1

Characteristic features of ALE, their implications on the film growth and the consequent practical advantages

Characteristic feature of ALE	Inherent implication on film deposition	Practical advantage
Self-limiting growth process	Film thickness is dependent only on the number of deposition cycles	Accurate and simple thickness control
	No need of reactant flux homogeneity	Large area capability Large batch capability Excellent conformality No problems with inconstant vaporization rates of solid precursors Good reproducibility Straightforward scale-up
Separate dosing of reactants	Atomic level control of material composition	Capability to produce sharp interfaces and superlattices Possibility to interface modification
	No gas phase reactions	Favors precursors highly reactive towards each other, thus enabling effective material utilization
Processing temperature windows are often wide	Sufficient time is provided to complete each reaction step	High quality materials are obtained at low processing temperatures
	Processing conditions of different materials are readily matched	Capability to prepare multilayer structures in a continuous process

sition process is based on alternating chemisorption of the precursors, surface reaction and desorption of the gaseous side-products. When carried out within certain temperature limits, i.e. in the 'ALE window', ALE is a self-limiting deposition process where the growth rate is independent of growth parameters like temperature, vapor pressure, precursor fluxes and pulse and purge times [12,16]. The characteristic features of ALE and their implications on the growth process and resulting film material are presented in Table 1.

### 3. ALE growth of binary oxides films

Table 2 summarizes the ALE processes used for depositing binary oxide films, either in a pure form or doped with a second cation or anion. In general the chemistry used in ALE is rather similar to that employed in CVD. There are, however, some basic differences. While in CVD highly reactive precursor combinations, e.g.  $\text{AlCl}_3$ ,  $\text{TiCl}_4$  or  $\text{ZrCl}_4$  together with water, are problematic because of premature gas phase reactions, in ALE these problems are inherently avoided due to separate dosing of the precursors. In fact, in an ALE process aggressively reacting precursors are desired because they facilitate the use of short pulse times and high precursor utilization efficiencies. Another important difference between ALE and CVD chemistries is that, since in ALE no constant reactant fluxes are required, the use of solid sources is easier than in CVD where changes in surface areas of solid sources may lead to inconstant vaporizing rates and, thus, complicate the growth rate control. As a consequence of these two features ALE is very versatile in respect of the precursor choices. It should be empha-

sized, however, that for each particular oxide only a limited number of precursor combinations may be used. For example, even though volatile metal chlorides and water are ideal ALE precursors for many oxides,  $\text{ZnCl}_2$  and  $\text{NbCl}_5$  cannot be employed in depositing the corresponding oxides. While  $\text{ZnCl}_2$  seems to suffer from a low reactivity with water, the problems related to  $\text{NbCl}_5$  arise from its tendency to etch  $\text{Nb}_2\text{O}_5$  [53]. Therefore it can be concluded that though some predictions can be drawn from other closely related materials, each process has to be examined on its own.

The role of the oxygen precursor may be twofold; it may either only supply the oxygen or it may also act as an oxidizing agent. The importance of the oxygen source is demonstrated by the growth of  $\text{Ga}_2\text{O}_3$  from  $\text{Ga}(\text{thd})_3$  and either oxygen, water or ozone [52]. While no growth took place with oxygen and the films deposited with water were heavily contaminated with carbon (about 30 at.%), those deposited with ozone which is a strong oxidizer contained only about 1 at.% carbon.

The temperature ranges given in Table 2 are those in which reasonable film growth was reported to take place without any major precursor decomposition leading to an uncontrolled growth. They do not, however, necessarily represent the 'ALE-window' [12], i.e. the temperature range where the growth rate, expressed in terms of thickness increment per cycle, would be independent of the temperature. In fact, it is rather common feature for many oxide processes that there does not exist any distinct ALE-window. This behavior arises from combined effects of several temperature dependent factors, the most important of which are kinetics of the surface reactions between the alternately supplied precursors, dehydroxylation of the surface and

Table 2

A summary of ALE processes used for depositing pure and doped binary oxide thin films

Material	Precursor combination	Temperature (°C)	Reference
Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub> + H <sub>2</sub> O/ROH/O <sub>2</sub>	100–660	[17–24]
	Al(OEt) <sub>3</sub> + H <sub>2</sub> O/ROH/O <sub>2</sub>	250–500	[21]
	Al(OPr) <sub>3</sub> + H <sub>2</sub> O/ROH/O <sub>2</sub>	250–500	[21]
	Al(CH <sub>3</sub> ) <sub>3</sub> + H <sub>2</sub> O/H <sub>2</sub> O <sub>2</sub> /N <sub>2</sub> O	100–600	[25–28]
TiO <sub>2</sub>	TiCl <sub>4</sub> + H <sub>2</sub> O/H <sub>2</sub> O <sub>2</sub>	100–600	[17,29–33]
	Ti(OEt) <sub>4</sub> + H <sub>2</sub> O	200–375	[31,34]
	Ti(O <sup>i</sup> Pr) <sub>4</sub> + H <sub>2</sub> O	150–350	[31,35,36]
Ta <sub>2</sub> O <sub>5</sub>	TaCl <sub>5</sub> + H <sub>2</sub> O	100–500	[22,23,37,38]
	Ta(OEt) <sub>5</sub> + H <sub>2</sub> O	150–450	[28,39]
In <sub>2</sub> O <sub>3</sub>	InCl <sub>3</sub> + H <sub>2</sub> O	400–500	[40,41]
SnO <sub>2</sub>	SnCl <sub>4</sub> + H <sub>2</sub> O	300–600	[42,43]
ZnO	Zn(CH <sub>3</sub> COO) <sub>2</sub> + H <sub>2</sub> O	290–360	[44]
	Zn(CH <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> O	150–250	[45]
	Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + H <sub>2</sub> O	120–350	[45]
MgO	Mg(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> + H <sub>2</sub> O	370–900	[46,47]
ZrO <sub>2</sub>	ZrCl <sub>4</sub> + H <sub>2</sub> O	300–500	[28,31,48]
HfO <sub>2</sub>	HfCl <sub>4</sub> + H <sub>2</sub> O	300–500	[23,28,31,49]
CeO <sub>2</sub>	Ce(thd) <sub>4</sub> + O <sub>3</sub>	350–425	[50]
Y <sub>2</sub> O <sub>3</sub>	Y(thd) <sub>3</sub> + O <sub>3</sub> /O <sub>2</sub>	425–500	[51]
Ga <sub>2</sub> O <sub>3</sub>	Ga(thd) <sub>3</sub> + O <sub>3</sub> /H <sub>2</sub> O	350–400	[52]

desorption or self-decomposition of the metal precursors [31]. In some cases also readsorption of reaction byproducts and etching of the film by the precursors may have a role [37,53].

At low temperatures the growth rate is often found to increase with temperature until the saturated level is reached [30,33,34,36,39,42,50] which is obviously due to thermal activation of the surface reactions between the two precursors. If too short exposure times are used these reactions are only partially completed within one cycle. With increasing temperature the degree of completion increases until the temperature is high enough for the reactions to proceed into saturation within the given cycle time. In principle, under these circumstances the growth rate per cycle could be increased also by giving more time for the reactions to occur but this would increase the total process time substantially.

In some cases, especially when water is used as an oxygen source, the growth rate has been found to decrease rather steadily with increasing temperature [20,29,32,38,45]. This decrease has usually been attributed to increasing dehydroxylation of the surface. After each water pulse the oxide surface is terminated with hydroxyl groups, and if sufficiently low temperatures are used also some molecular water may be present. During the subsequent reaction step these species will act as preferential reactive sites for the incoming metal precursors. When the temperature is increased water and hydroxyl groups will exhibit an increasing tendency to desorb from the surface before the other precursor is dosed in. Nevertheless, since the different species, i.e. molecularly chemisorbed water and bridging and terminal hydroxyl groups which may

further be isolated or hydrogen bonded, are desorbed at different temperatures the density of reactive sites will decrease only gradually with increasing temperature [54], thus explaining the observed gradual decrease of the growth rate.

At high temperatures the growth rate may exhibit a gradual or sudden increase because of the thermal self-decomposition of the metal precursor [34,36,39]. On the other hand, if strong decomposition occurs already before the substrates the precursor flux arriving on the substrates may be significantly decreased thereby causing a decrease of the growth rate. When self-decomposition takes place, the self-control of the ALE growth will evidently be lost. Nevertheless, in some cases minor self-decomposition may be tolerated without losing the advantageous features of ALE [34]. This requires that the decomposition product is the same as the one resulting from the reactions between the two precursors, and that the decomposition rate is uniform over the whole substrate. Obviously, the latter requirement is met only when the decomposition process is surface reaction rate controlled.

#### 4. Conformality

Due to its surface-controlled nature the ALE process has a great potential for step coverage and conformal coating which are often required in thin film device processing. However, there are only a few documented cases where this inherent advantage of the ALE process has been demonstrated [26].

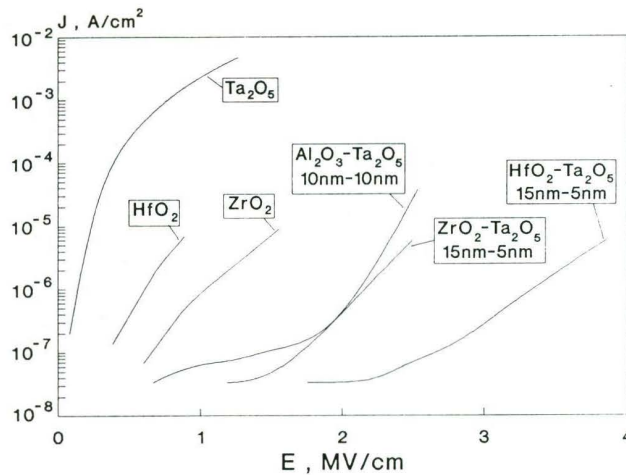


Fig. 1. Leakage current densities vs. electric fields for some selected single layer and multilayer structures. In all cases the total thickness of the dielectric film was about 160 nm [28].

Very recently, Düscö et al. [55] have deposited tin oxide into porous silicon which represents an extreme case for conformal coatings, with a pore depth of 2  $\mu\text{m}$  and an average pore diameter of 14 nm the aspect ratio is as high as 140:1. Using RBS, SIMS and XTEM the authors presented evidence for conformal coating of the pores with  $\text{SnO}_2$  originating from the exchange reaction between adsorbed  $\text{SnCl}_4$  and  $\text{H}_2\text{O}$  [42]. The experimental conditions must be carefully chosen because the surface controlled ALE process in the pores may easily turn into a CVD process.

## 5. Multilayers

Owing to the inherent layerwise processing and the possibility to match deposition temperatures of different materials (Tables 1 and 2), ALE is an attractive technique for preparation of multilayer structures. Already in the first application of ALE, i.e. in manufacturing of TFEL displays [12], the multilayer processing capability was, and still is, successfully utilized at two different thickness levels. First, the heart of the TFEL device, the three layer structure dielectric-semiconductor-dielectric is deposited in one continuous ALE process which thereby both fastens and simplifies the production and improves the interface quality. While 0.5 to 1  $\mu\text{m}$  thick zinc or alkaline earth sulfides doped with manganese or rare earths are employed as the semiconducting phosphors, the dielectric layers having thicknesses of about a few hundred nanometers consist of either  $\text{Al}_2\text{O}_3$  or  $\text{Al}_x\text{Ti}_y\text{O}_z$  [12,56]. The latter material also represents the second level of multilayer processing in ALE manufacturing of the TFEL devices. Even though the pure ALE grown  $\text{Al}_2\text{O}_3$  is capable of withstanding the high alternating electric fields, about 2 MV

$\text{cm}^{-1}$  applied across the dielectric-semiconductor-dielectric structure, even better results have been achieved by preparing multilayer structures where thin  $\text{TiO}_2$  layers are incorporated into the  $\text{Al}_2\text{O}_3$  film [12,17].

Because of the good results gained from the  $\text{Al}_2\text{O}_3$  based composite dielectrics, the multilayer approach has recently been examined also with some other ALE grown insulating oxides, especially with  $\text{Ta}_2\text{O}_5$ . As typical of  $\text{Ta}_2\text{O}_5$  films irrespective of the deposition method, also the ALE grown  $\text{Ta}_2\text{O}_5$  films are relatively leaky in their as-deposited form. Under 1  $\text{MV cm}^{-1}$  electric field leakage currents of about 40 and 2  $\text{mA cm}^{-2}$  have been measured for  $\text{Ta}_2\text{O}_5$  films grown from  $\text{TaCl}_5$  [22,23] and tantalum ethoxide [39], respectively, using water as the oxygen source. These high leakage current values prohibit the use of pure  $\text{Ta}_2\text{O}_5$  films as dielectric materials in TFEL devices. By preparing sandwich structures consisting of  $\text{Ta}_2\text{O}_5$  and another oxide, i.e.  $\text{HfO}_2$ ,  $\text{ZrO}_2$  or  $\text{Al}_2\text{O}_3$ , the leakage current densities were drastically reduced (Fig. 1) [22,23,28]. The most attractive results were obtained with the  $\text{Ta}_2\text{O}_5$ - $\text{HfO}_2$  and  $\text{Ta}_2\text{O}_5$ - $\text{ZrO}_2$  multilayers in which the low leakage current densities were accompanied by high and essentially constant dielectric permittivities around 20. The lowest leakage current measured at 2  $\text{MV cm}^{-1}$  was only  $3 \times 10^{-8} \text{ A cm}^{-2}$  which is an extremely low value for a film which has not experienced temperatures higher than 325°C. In the optimized structures the thicknesses of the single oxide layers were 5–15 nm [28].

The multilayer processing capability together with the accurate and simple thickness control make ALE a potential technique for optical applications. Recently ALE preparation of some basic optical dielectric multilayer components was demonstrated by Riihelä et al. [57]. Using  $\text{Al}_2\text{O}_3$  and  $\text{ZnS}$  as the low and high refrac-



tive index materials, respectively, antireflection coatings, neutral beam splitters, high reflection coatings and Fabry–Perot filters were prepared. The most complicated structure consisted of 20 layers, each having an optical thickness of one quarter of the central wavelength 580 nm which means that the geometrical thicknesses of the  $\text{Al}_2\text{O}_3$  and ZnS films were 86 and 62 nm, respectively. The accuracy of the film deposition was verified by comparing the measured transmission and reflectance spectra with those calculated for the ideal structures (Fig. 2).

Though with III-V compounds the layerwise ALE processing has been successfully taken down to an atomic level in growing superlattices [12], with oxide materials no such structures have yet been prepared. This is mainly due to the fact that the great majority of the oxide studies have concentrated on amorphous or polycrystalline rather than epitaxial films. Even if epitaxial oxide films were deposited, it might be difficult to prepare superlattices with an exact atomic level accuracy because the growth rates are usually lower than the one monolayer per cycle. On the other hand, though this evidently has not resulted in continuous monolayers, the atomic level processing has been utilized with polycrystalline oxide films in their controlled doping with third ions, as will be discussed in the following section.

## 6. Doping of oxides

Transparent conducting oxides represent very important large area applications to optoelectronics, e.g. transparent electrodes in flat displays and solar cells. All the most common transparent conducting oxides have been prepared by ALE by doping the binary oxides to enhance their conductivity. Even though the dopant could be introduced also together with the host

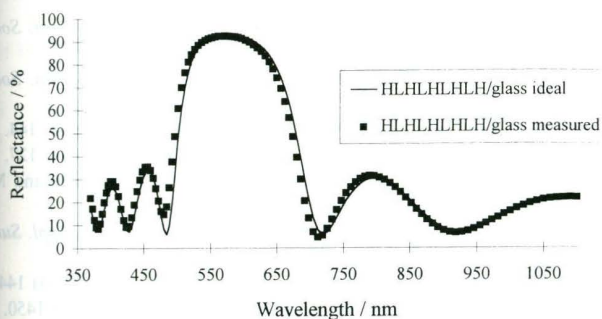


Fig. 2. Reflectance spectra of a nine layer structure HLHLHLHLH/glass, where H and L refer to high refractive index ZnS and low refractive index  $\text{Al}_2\text{O}_3$  layers whose optical thickness are one quarter of the central wavelength 580 nm. The ideal spectrum was calculated for a structure where all the film parameters were set to their target values [57].

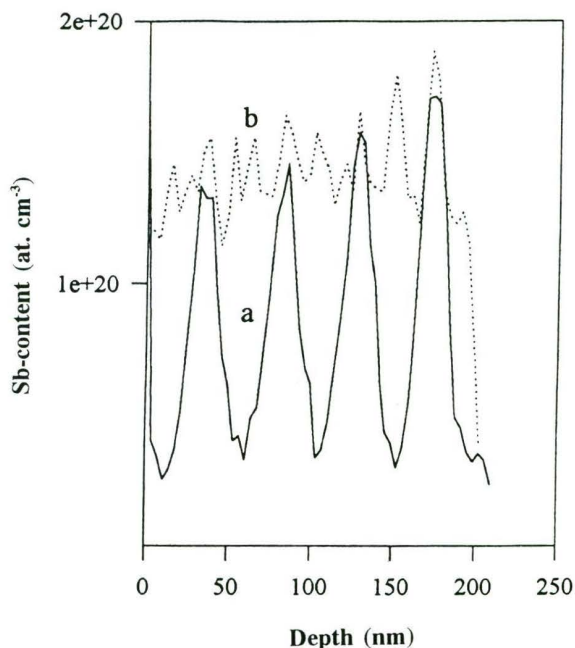


Fig. 3. A depth distribution of antimony in  $\text{SnO}_2$ :Sb films prepared by using pulsing sequence ratios  $(\text{SbCl}_5 + \text{H}_2\text{O}):(\text{SnCl}_4 + \text{H}_2\text{O})$  1:1200 (a) and 1:600 (b) [58].

precursors, a more common way is to supply the dopant precursor as a separate pulse. Tin has been incorporated into indium oxide layers to form conducting indium tin oxide (ITO) using chlorides as the metal precursors [41]. Similarly, although at a lower concentration level, antimony enhances the conductivity of tin dioxide [43]. SIMS depth profiling indicate a controlled doping even at a very low level where one  $\text{SnCl}_4 + \text{H}_2\text{O}$  cycle out of 1200 is replaced by a  $\text{SbCl}_5 + \text{H}_2\text{O}$  cycle (Fig. 3) [58]. Likewise, ZnO has been doped with aluminium using organometallic compounds and water as precursors [45]. The lowest resistivities measured for these transparent conducting oxide films were  $2 \times 10^{-4} \Omega \text{ cm}$  for  $\text{In}_2\text{O}_3$ :Sn [41],  $1 \times 10^{-3} \Omega \text{ cm}$  for  $\text{SnO}_2$ :Sb [43] and  $8 \times 10^{-4} \Omega \text{ cm}$  for ZnO:Al [45].

## 7. Ternary and quaternary compounds

In contrast to CVD, the application of ALE has been almost exclusively focused on binary systems, viz. metal oxides, nitrides and sulfides. Very recently, however, considerable progress has been made with the perovskite-type oxides. As an expansion of bulk material studies Seim et al. [59] have prepared  $\text{LaNiO}_3$  from beta-diketonate type precursors and oxygen.  $\text{LaNiO}_3$  exhibits a range of interesting properties for possible applications because it is a metallic conductor and has Pauli type paramagnetic behaviour. The thin films were

deposited at 200–400°C but enhancing crystallinity and electrical conductivity requires annealing at 600°C. Preliminary results show that another perovskite oxide LaCoO<sub>3</sub> can be deposited by a similar process.

The new high- $T_c$  superconductors represent a more difficult case because in the case of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, for instance, the deposition of three metallic constituents must take place in the same temperature range and, furthermore, the oxygen concentration must be controlled. The problem of in situ deposition is largely related to precursor chemistry because the choice of precursors for yttrium and especially for barium is limited. Nevertheless, Mölsä [60] was able to deposit by ALE at 450°C YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> films which exhibited superconductivity after oxygen annealing. Layer-by-layer growth has been reported by other groups as well [61].

## 8. Conclusions

ALE has demonstrated its capabilities for controlled processing of oxide thin films for large area applications. Besides pure oxides examples of ALE also include doped materials and layered structures. Although most work has been carried out with binary compounds, there are recent reports on ternary phases also. The perovskite thin films open up new applications for ALE. Further developments are, in most cases, depending on precursor and reactor designs.

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