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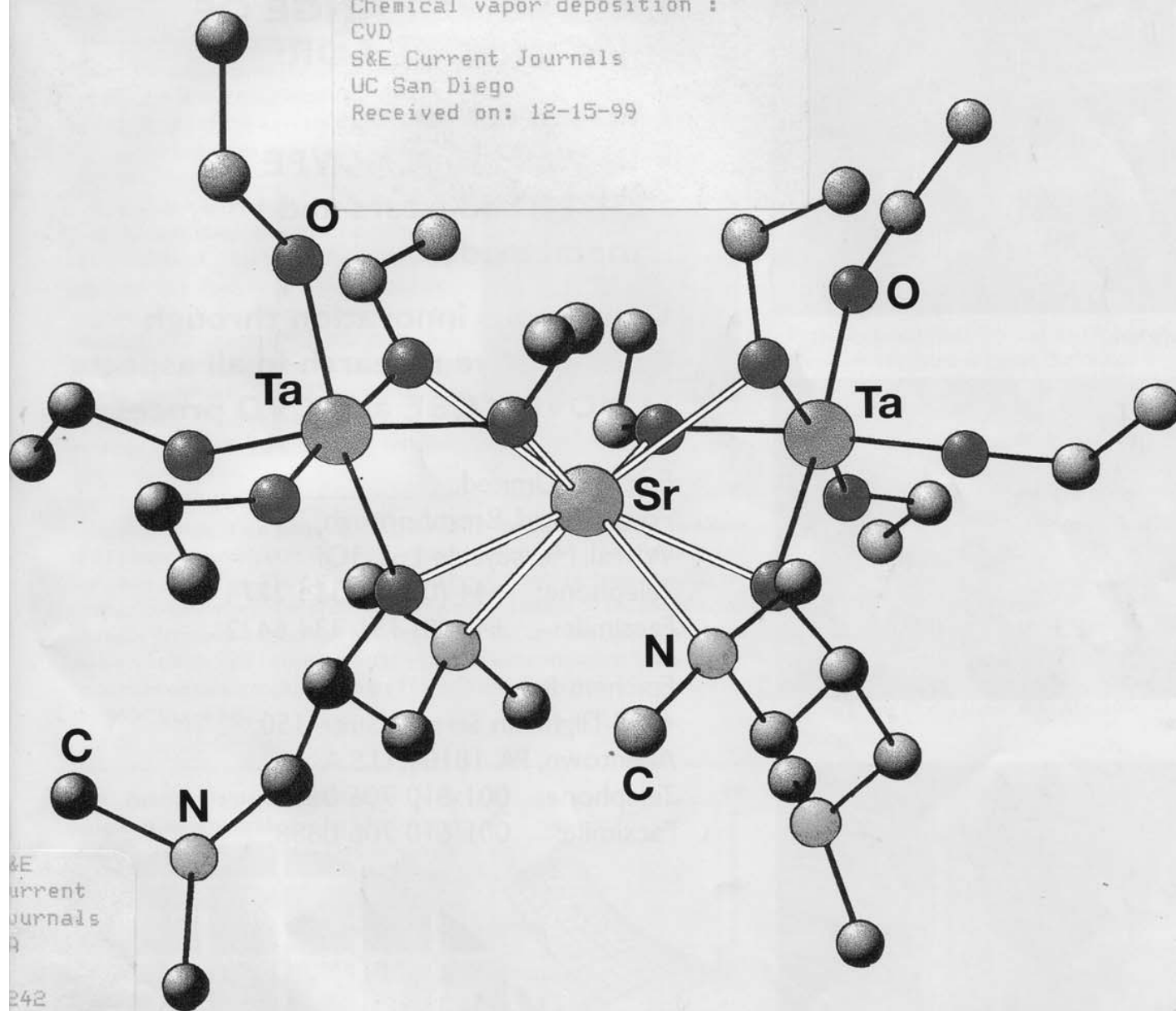
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No. 1

Novel Precursors for MOCVD of Strontium Tantalate

CVD of Pyrocarbon from Propane: Gas-Phase Analysis

Nanostructured Composite TiO_2 -Pt Thin Films

Conformal TiN and Al_2O_3 by ALE

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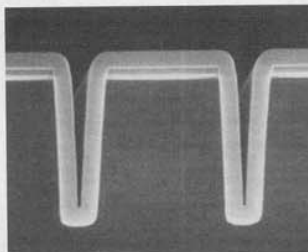
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Cover: The cover shows the molecular structure of the novel bimetallic compound $[\text{Sr}\{\text{Ta}(\text{OEt})_5(\text{bis-dmap})\}_2]$, which contains the nitrogen donor functionalized ligand bis(dimethylamino) iso-propoxide, $\text{OCH}(\text{CH}_2\text{NMe}_2)\text{CH}_2\text{NMe}_2$ (bis-dmap). Full details of the use of this novel bimetallic alkoxide precursor for MOCVD of strontium tantalate films are to be found in the article by Jones et al. on page 9.

Communication: Perfectly conformal deposition into deep trenches or filling of them without keyhole formation is achieved (see Figure) by atomic layer deposition (ALD). Good conformality can be obtained with other CVD processes, but the unique surface-controlled, self-limiting growth mechanism of ALD may give the technique significant advantages over other methods for future generation IC technology.



M. Ritala,* M. Leskelä,* J.-P. Dekker,
C. Mutsaers, P. J. Soininen, J. Skarp

Chem. Vap. Deposition **1999**, 5, 7 ... 9

Perfectly Conformal TiN and Al_2O_3 Films
Deposited by Atomic Layer Deposition

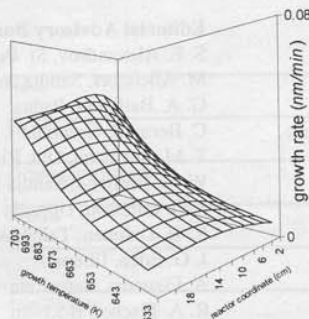
Communication: Thin films of the perovskite strontium bismuth tantalate (SBT) have a large potential application as capacitors in non-ferroelectric computer memories. The MOCVD of SBT has, however, been severely restricted by lack of suitable precursors. This paper reports on the use of novel alkoxide precursors containing both strontium and tantalum (see cover) and shows that with liquid injection MOCVD, crystalline strontium tantalate can be formed on annealing the deposited layer. This is a promising approach for the MOCVD of SBT.

M. J. Crosbie, P. J. Wright, H. O. Davies,
A. C. Jones,* T. J. Leedham, P. O'Brien,
G. W. Critchlow

Chem. Vap. Deposition **1999**, 5, 9 ... 12

MOCVD of Strontium Tantalate Thin
Films Using Novel Bimetallic Alkoxide
Precursors

Full Paper: Multicomponent films with unique nanostructures can be ideally prepared by CVD. Here the CVD of composite nanostructured TiO_2 -Pt films, with controllable composition and Pt gradient, have been prepared from metal-organic precursors. Deposition kinetics have been investigated. The Figure shows a simulation for TiO_2 growth as a function of temperature and reactor coordinate.



G. A. Battiston,* R. Gerbasi, M. Porchia,
A. Gasparotto

Chem. Vap. Deposition **1999**, 5, 13 ... 20

Metal Organic CVD of Nanostructured
Composite TiO_2 -Pt Thin Films: A Kinetic
Approach

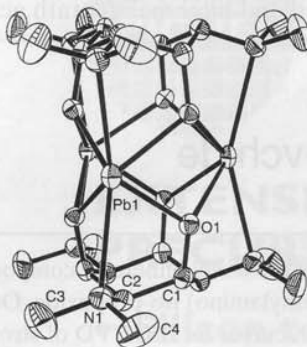
Full Paper : Kinetically controlled CVD of the oxides of copper is governed by an intriguing interplay. In this work it is conclusively shown that Cu_2O deposition is controlled by a Langmuir–Hinshelwood mechanism involving non-competitively adsorbed reagents. The formation of CuO is significantly slower than Cu_2O even though it is a less activated process. A model based on the reversible adsorption of molecular $[\text{Cu}(\text{acac})_2]$ has been used to explain the observed deposition behavior for both oxides.

G. G. Condorelli, G. Malandrino,
I. L. Fragalà*

Chem. Vap. Deposition **1999**, *5*, **21** ... 27

Kinetic Study of MOCVD Fabrication of Copper(I) and Copper(II) Oxide Films

Full Paper: Lead(II) oxide has interesting semiconductor and photoconducting properties with important industrial applications. This paper describes MOCVD using a trinuclear precursor (see Figure) that despite its high molecular weight can be transported into the reactor and form metallic or oxide deposits. The nature of the films depends on the type of substrate, with the oxides being of potential interest.



R. Hedinger, T. Kradolfer,
K. Hegetschweiler,* M. Wörle,
K.-H. Dahmen*

Chem. Vap. Deposition **1999**, *5*, **29** ... 35

The Deposition of Pb and PbO on Various Substrates by MOCVD Using a New Trinuclear Lead Precursor

Full Paper: Chemical vapor infiltration (CVI) of pyrocarbon is a widely used technique for the production of carbon–carbon composites. Few studies have been made, though, of the gas phase pyrolysis of hydrocarbons at the high temperatures required for CVI. Here results from a combined FTIR and mass spectrometric analysis of the thermal decomposition of propane are presented. On the basis of the experimental results some realistic pathways are proposed to explain the observed maturation of the gas phase.

O. Féron, F. Langlais, R. Naslain*

Chem. Vap. Deposition **1999**, *5*, **37** ... 47

Analysis of the Gas Phase by In Situ FTIR Spectrometry and Mass Spectrometry During the CVD of Pyrocarbon from Propane

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Communications

Perfectly Conformal TiN and Al₂O₃ Films Deposited by Atomic Layer Deposition**

By Mikko Ritala,* Markku Leskelä,* Jan-Pieter Dekker, Cees Mutsaers, Pekka J. Soininen, and Jarmo Skarp

The prevailing development trends in integrated circuit technology have placed ever increasing demands on thin film deposition techniques. The continuous decrease in the size of devices and increase of design complexity require nearly perfect conformality and accurate film thickness control. The increase of the wafer size, in turn, calls for large area uniformity. A potential thin film deposition technique for meeting these requirements in the future beyond the capabilities of the presently used techniques is atomic layer deposition (ALD), widely known also as atomic layer epitaxy (ALE).^[1–5] ALD was originally introduced for the manufacture of thin film electroluminescent displays,^[6] where it has been used commercially already for more than a decade.^[1,2] ALD is a special modification of the chemical vapor deposition (CVD) technique with the distinctive feature of the alternate and cyclic supply of the gaseous precursors to the substrates.^[1–4] During each exposure step the incoming precursor chemisorbs or reacts with the surface saturatively, and the subsequent purging step removes the excess precursor and reaction byproducts before the introduction of the other precursor. The key feature of the ALD method is the saturation of all the reaction and purging steps, which makes the film growth self-limiting. As a consequence, large area uniformity and conformality are inherently obtained, and film thicknesses are simply and accurately controlled by the number of deposition cycles.

Evidence of the vast potential of ALD for excellent conformality include uniform surface modification of porous silicon layers^[7,8] and high surface area silica and alumina powders,^[9–11] and modification of the pore size of porous alumina membranes.^[12] Nevertheless, studies on the conformality of ALD or ALE films on features with dimensions relevant to microelectronic devices are sparse.^[13] In this work, we have verified the perfect conformality of two

ALD processes of a potential interest to microelectronics, i.e., TiN and Al₂O₃. In addition, with the latter material also large area uniformity is demonstrated.

The TiN^[14,15] and Al₂O₃^[16–21] ALD processes used in this work have been described earlier and examined in detail with respect to film growth and basic film properties. Briefly, polycrystalline TiN films were deposited from TiCl₄, Zn, and NH₃ at 500 °C at a rate of 0.2 Å/cycle and amorphous Al₂O₃ films from trimethylaluminum (TMA, Al(CH₃)₃) and water at 300 °C at a rate of about 1.1 Å/cycle. Both processes result in pure films containing less than 0.1 at.-% chlorine, zinc, and carbon residues, but the TiN films become easily oxidized when exposed to air and thus contain a few atomic percent oxygen. In the growth of TiN, zinc was used as an additional reducing agent because it has a beneficial effect on the film resistivity decreasing it to about 50 μΩ cm as compared to 250 μΩ cm achieved using only TiCl₄ and NH₃. Al₂O₃ films have a refractive index of 1.666, permittivity of about 8, and leakage current densities through them are in the order of 10^{–6} A/cm² at an applied electric field of 2 MV/cm.

Representative cross-sectional scanning electron microscopy (SEM) images of TiN and Al₂O₃ films deposited onto patterned silicon substrates are shown in Figures 1 and 2. While examining these images it should be recognized that on top of the silicon wafer there is a 100 nm thick thermal silicon oxide layer, even if in some cases it might be hard to distinguish this layer from the TiN or Al₂O₃ films. Keeping this in mind, it may be concluded that, within the accuracy of the images, a perfect 100 % conformality has been achieved in all the trenches. Also the preservation of the original well-defined, nearly straight angles between the walls and the bottom of the trenches should be noted (Figs. 1a and 2a). No keyhole formation is observed even in those cases where the trenches have become completely or nearly filled (Figs. 1c and 2b). Furthermore, Figure 1c indicates that after the trenches have become filled, the film surface continues its evolution towards, eventually, complete planarization, which could be expected if the film was made thick enough in comparison with the trench dimensions. The only observable difference between TiN and Al₂O₃ is that the former exhibits some roughness due to its polycrystalline structure^[14,15] whereas Al₂O₃ is amorphous.^[19]

The TiN films were made with a small research scale reactor where the inlets of the separate precursor flow channels are very close to the substrates, and therefore the film growth on the first half of the substrate is somewhat disturbed by various kinds of secondary processes.^[14] These secondary processes are all reactor design related. As a consequence, in this region the film thickness is not uniform but decreases in the flow direction, and only on the latter half of

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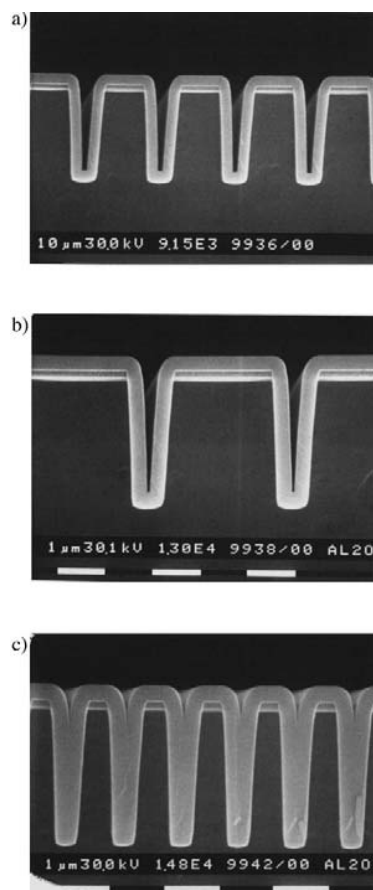


Fig. 1. Representative cross-sectional SEM images of 300 nm thick Al_2O_3 films deposited on Si wafers with trench structures.

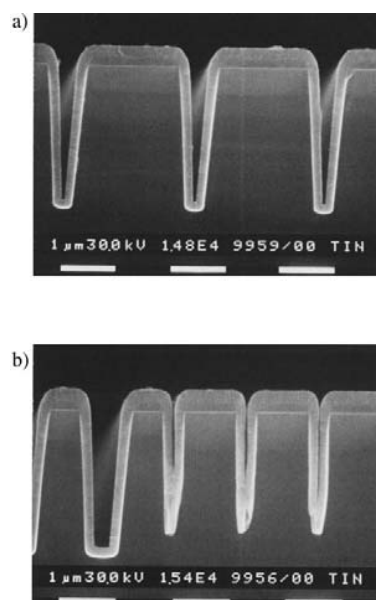


Fig. 2. Cross sections of 160 nm TiN films on a patterned substrate.

the substrate is uniform film obtained.^[14] By contrast, the Al_2O_3 films were deposited using a reactor where the substrates are much further away from the precursor inlets, and thus the secondary processes have no effect on the film uniformity. The thickness uniformity of Al_2O_3 films was analyzed by comparing three 150 mm wafers, two of which were processed in the same run and the third one in the next run, both runs consisting of 2730 cycles for depositing about 300 nm thick film. These measurements indicated less than 0.7 % standard deviation both within a single wafer and in comparison between the three wafers (Table 1). The difference between the maximum and minimum thicknesses on one wafer was at maximum 1.4 %.

Table 1. Average thicknesses (d_{avg}), standard deviations (d_{rms}), and differences between maximum and minimum thicknesses ($d_{\text{max}} - d_{\text{min}}$) for Al_2O_3 films deposited on three 150 mm wafers. Film thicknesses were measured by an ellipsometer from five positions on each wafer, one in the middle and four close to the wafer edges so that the measuring points formed a cross-like pattern. The refractive index of the Al_2O_3 films was 1.666 at the ellipsometer wavelength.

	Run 1, Wafer 1	Run 1, Wafer 2	Run 2, Wafer 1	All wafers
d_{avg} [nm]	295.8	297.9	298.7	297.5
d_{rms} [nm]	2.0	0.91	0.66	1.80
$d_{\text{rms}}/d_{\text{avg}}$ [%]	0.66	0.31	0.22	0.61
$d_{\text{max}} - d_{\text{min}}$ [nm]	4.4	2.5	1.6	6.3
$(d_{\text{max}} - d_{\text{min}})/d_{\text{avg}}$ [%]	1.4	0.84	0.54	2.1

In conclusion, the perfect conformality of two thin film materials, TiN and Al_2O_3 , deposited by ALD was demonstrated. The surface-controlled, self-limiting film growth mechanism of ALD makes it possible to deposit films uniformly into deep trenches, and the trenches may also be filled completely without keyhole formation. Though good conformality is obtained also by other processes, such as CVD, when operated in surface-controlled mode, unique to ALD is that these conditions are inherently ensured by the alternate precursor supply and the self-limiting growth mechanism. This excellent conformality may give ALD a great advantage over the other thin film deposition techniques for the future generation IC technology. Also the good large-area uniformity resulting from the ALD process was evidenced by observing less than 0.7 % standard deviations in thicknesses of Al_2O_3 films deposited onto 150 mm silicon wafers.

Experimental

TiN films were grown at 500 °C from TiCl_4 , Zn, and NH_3 using a small scale F-120 research ALE reactor [2] (Microchemistry Ltd., Espoo, Finland) incorporating two $5 \times 5 \text{ cm}^2$ substrates as described earlier [14,15]. Al_2O_3 films were deposited at 300 °C with the R&D and pilot scale F-450 ALE reactor [22] (Microchemistry Ltd., Espoo, Finland) using trimethylaluminum (TMA , $\text{Al}(\text{CH}_3)_3$) and water as precursors. The maximum substrate size of this reactor is $40 \times 30 \text{ cm}^2$ or 300 mm in diameter. The reactors were operated under a pressure of about 10 mbar using nitrogen (99.999 %) as a carrier and purging gas. TiCl_4 , NH_3 , TMA, and H_2O were pulsed into the reac-

tors from their external sources using solenoid or pneumatic valves. Zn was evaporated inside the reactor at 440 °C and pulsed onto the substrates by means of inert gas valving [2]. In the TiN process the exposure times were 0.2 s for TiCl_4 and Zn, and 0.5 s for NH_3 , and all the purge times were 0.5 s. These values are the same as those optimized in experiments made on planar substrates, i.e., no special attention was paid to the potential need for longer exposure and purging times in order to transport precursors into and out of the high aspect ratio trenches. For the deposition of Al_2O_3 , 1.5 s TMA and H_2O exposure times and 3.0 s purge periods were used.

The substrates used for the Al_2O_3 films were 150 mm silicon wafers covered by about 100 nm thick thermal silicon oxide film. Trench structures with varying aspect ratios were prepared by standard patterning techniques. For the growth of TiN, $5 \times 5 \text{ cm}^2$ pieces were cut from these substrates.

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MOCVD of Strontium Tantalate Thin Films Using Novel Bimetallic Alkoxide Precursors**

By Michael J. Crosbie, Peter J. Wright, Hywel O. Davies, Anthony C. Jones,* Timothy J. Leedham, Paul O'Brien, and Gary W. Critchlow

Thin films of the layered perovskite strontium bismuth tantalate, $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT), have a large potential application as capacitor layers in non-volatile ferroelectric computer memories.^[1,2] In contrast to capacitors based on other ferroelectric oxides, such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$, those based on SBT show negligible polarization fatigue, are fully compatible with conventional Pt-electrode technology, and maintain good electrical properties, even when very thin.^[2]

SBT thin films have been deposited by a variety of techniques, including sol-gel,^[3] metal-organic decomposition,^[4,5] pulsed laser ablation,^[6] and metal-organic chemical vapor deposition (MOCVD).^[7-9] MOCVD has a number of advantages over other deposition techniques as it offers the potential for large area growth, good film uniformity and composition control, and excellent conformal step coverage at device dimensions $< 2 \mu\text{m}$. The MOCVD technique is also fully compatible with existing silicon CVD processes.

The MOCVD of SBT has thus far been severely restricted by a lack of suitable metal-organic precursors. Conventional precursors^[7-9] include $\text{Sr}(\text{thd})_2$ (where thd = 2,2,6,6-tetramethyl-3,5-heptanedionate), $\text{Bi}(\text{C}_6\text{H}_5)_3$ and $\text{Ta}(\text{OEt})_5$ or $\text{Ta}(\text{O}^i\text{Pr})_4(\text{thd})$, which are generally incompatible, having very different physical properties and decomposition characteristics. A potential solution to this problem is the use of "single-source" precursors, which contain the elements required in the oxide film in a single stoichiometric compound, and the Sr/Ta alkoxide $[\text{Sr}(\text{Ta}(\text{O}^i\text{Pr})_6)_2]$ has recently been investigated as a precursor to SBT.^[10] A potential advantage of single-source precursors is that the metal/metal ratio in the precursor matches that in the deposited oxide film, and this approach has been successfully



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