# Nanostructured ZrO<sub>2</sub> and Zr-C-N Coatings from Chemical Vapor Deposition of Metal-Organic Precursors

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Dedicated to Professor Michael Veith on the Occasion of his 60<sup>th</sup> Birthday

Abstract. Nanocrystalline zirconium carbonitride (Zr-C-N) and zirconium oxide (ZrO<sub>2</sub>) films were deposited by chemical vapor deposition (CVD) of zirconium-tetrakis-diethylamide (Zr(NEt<sub>2</sub>)<sub>4</sub>) and -tert-butyloxide (Zr(OBu<sup>t</sup>)<sub>4</sub>), respectively. The films were deposited on iron substrates and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The Zr-C-N films show blue, golden brown or bronze colours, with colour stability depending upon the precursor composition (pure metal amide or mixed with Et<sub>2</sub>NH). The deposition temperature showed no pronounced effect on the granular morphology of the Zr-C-N films. The XRD data of the films correspond to the formation of carbonitride phase whereas the XPS analyses revealed a strong surface oxidation and incorporation of oxygen in the film. The films deposited using a mixture of Zr(NEt<sub>2</sub>)<sub>4</sub> and Et<sub>2</sub>NH showed higher N content, better adhesion and scratch resistance when compared to films obtained from the CVD of pure Zr(NEt<sub>2</sub>)<sub>4</sub>. Subject to the precursor composition and deposition temperature (550–750 °C), the microhardness values of Zr-C-N films were found to be in the range 2.11-5.65 GPa. For ZrO<sub>2</sub> films, morphology and phase composition strongly depend on the deposition temperature. The CVD deposits obtained at 350 °C show tetragonal ZrO<sub>2</sub> to be the only crystalline phase. Upon increasing the deposition temperature to 450 °C, a mixture of tetragonal and monoclinic modifications was formed with morphology made up of interwoven elongated grains. At higher temperatures (550 and 650 °C), pure monoclinic phase was obtained with facetted grains and developed texture.

Keywords: Zirconium; Nanostructured thin films; Chemical vapor deposition; Molecular precursors; Zirconium carbonitride; Zirconium oxide

# Nanostrukturierte ZrO<sub>2</sub> und Zr-C-N Beschichtungen durch chemische Gasphasenabscheidung von metallorganischen Precursoren

Inhaltsübersicht. Mittels chemischer Gasphasenabscheidung (CVD) wurden nanokristalline Zirconiumcarbonitrid (Zr-C-N)- und Zirconiumoxid (ZrO2)-Schichten aus Zirconium-tetrakis-diethylamid (Zr(NEt<sub>2</sub>)<sub>4</sub>) bzw. -tert-butyloxid (Zr(OBu<sup>t</sup>)<sub>4</sub>) hergestellt. Die Schichten wurden auf Eisensubstraten abgeschieden und mit Hilfe von Rasterelektronenmikroskopie (REM), Röntgendiffraktometrie (XRD) und X-ray-Photoelektronenspektroskopie (XPS) untersucht. Die Zr-C-N-Schichten zeigen blaue, gold-braune oder bronzene Farben, deren Stabilität von der Precursorzusammensetzung (reines Metallamid oder Gemisch mit Et<sub>2</sub>NH) abhängt. Außerdem besitzen sie eine granulare Morphologie, die jedoch keine deutliche Veränderung in Abhängigkeit von Abscheidetemperatur und Precursorzusammensetzung zeigt. Die XRD Daten dieser Schichten entsprechen der Bildung einer kubischen Carbonitridphase. Die XPS Analysen weisen auf eine starke Oberflächenoxidation sowie die Sauerstoffeinlagerung innerhalb der Schicht hin. Die Schichten,

die aus einem Gemisch von Zr(NEt<sub>2</sub>)<sub>4</sub> und Et<sub>2</sub>NH hergestellt wurden, haben, im Vergleich zu den durch CVD aus reinem Zr(NEt<sub>2</sub>)<sub>4</sub> erhaltenen Beschichtungen, einen höheren N-Gehalt und zeigen bessere Haftung sowie eine geringere Rissbildung im Scratch-Test. Für die Mikrohärte der Zr-C-N-Schichten wurden in Abhängigkeit von der Zusammensetzung und Abscheidetemperatur (550-750 °C) Werte zwischen 2,11-5,65 GPa gefunden. Für die ZrO<sub>2</sub>-Schichten besteht eine starke Abhängigkeit der Morphologie und Phasenzusammensetzung von der Substrattemperatur. Die bei 350 °C abgeschiedenen CVD-Filme bestehen ausschließlich aus der tetragonalen ZrO<sub>2</sub>-Phase. Bei Erhöhung der Substrattemperatur auf 450 °C entsteht ein Gemisch aus der tetragonalen und monoklinen Modifikation mit einer faserigen Morphologie. Bei höheren Temperaturen (550 und 650 °C) wurde eine reine monokline Phase mit facettierten Teilchen definierter Textur erhalten.

## Introduction

The coatings of transition metal oxides, nitrides and carbides are finding extensive applications due to their interesting properties such as high melting points, extreme hardness, chemical inertness and electrical conductivity [1-8]. The high dielectric constant of  $ZrO_2$  (~ 20, five times that of SiO<sub>2</sub>) makes it a potential candidate for gate dielectrics in metal oxide semiconductor field effect transistors (MOS-FETs) [7]. Similarly, zirconium nitrides (ZrN) and carbonitrides (Zr-C-N) are being used as decorative and protective coatings [9] due to their optical and mechanical properties, respectively [10-15]. Given the technological potential of nanostructured coatings, a number of variations of physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques have been used to deposit zirconium oxide, nitride, carbide and carbonitride films [16-19].

The CVD process based on the decomposition of ZrCl<sub>4</sub> in the presence of oxygen  $(ZrO_2)$ , nitrogen (ZrN) or carbon (ZrC) sources requires high temperatures for the chemical reaction to occur, which restricts the choice of the substrate materials. The deposition of these phases can be realized at relatively low temperatures by using PVD techniques, however it is limited in terms of compositional homogeneity and conformal coverage on complex geometries. In contrast to the inorganic precursors (e.g.,  $Zr(NO_3)_4$ ,  $ZrX_4$  (X = Cl, I)) that generally exhibit low vapor pressure and strong ionic bonding, the application of metal-organic precursors in the CVD process is capable of providing uniform films at reduced deposition temperatures due to the low binding energy in metal-organic compounds [20]. The formation of  $ZrO_2$  and Zr(C,N) from a variety of zirconium alkoxide and amide derivatives, respectively has been investigated on silicon substrates by thermal or plasma enhanced CVD processes [3, 21-25]. We report here on the low pressure CVD of zirconium carbonitride and oxide phases from zirconium-tetrakis-diethylamide (Zr(NEt<sub>2</sub>)<sub>4</sub>) and -tert-butyloxide (Zr(OBu<sup>t</sup>)<sub>4</sub>) precursors on steel substrates and the characterization of the CVD deposits.

# Experimental

## Synthesis of Precursors

The synthesis of  $Zr(NEt_2)_4$  (1) and  $Zr(OBu^t)_4$  (3) precursors and further experimental manipulations were performed in a modified Schlenk type vacuum assembly, taking stringent precautions against atmospheric moisture. All solvents were purified by standard methods and stored over appropriate desiccating agents. Anhydrous  $ZrCl_4$  (Aldrich) was dried in vacuum (100 °C/10<sup>-2</sup> Torr) to

\* Dr. habil. Sanjay Mathur Leibniz-Institut für Neue Materialien Im Stadtwald, Geb. 43A D-66041 Saarbrücken/Germany Tel: +49-681-9300-274/338 Fax: +49-681-9300-279 E-mail: smathur@inm-gmbh.de remove any residual water. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in benzene- $d_6$  on a NMR spectrometer AC 200 (Bruker). The compounds zirconium *tetrakis*-diethylamide (Zr(NEt<sub>2</sub>)<sub>4</sub>) and *tert*-butyloxide (Zr(O'Bu)<sub>4</sub>) were prepared following the published procedures [26–27]. Zr(NEt<sub>2</sub>)<sub>4</sub> was synthesized by a metathesis reaction of lithium diethyl amide (prepared from n-BuLi and Et<sub>2</sub>NH, eq. (1)) with zirconium chloride (eq. (2)) whereas Zr(O'Bu)<sub>4</sub> was obtained by a ligand exchange reaction of Zr(NEt<sub>2</sub>)<sub>4</sub> with excess Bu<sup>4</sup>OH as shown in eq. (3) [26–28].

$$Et_2NH + BuLi \xrightarrow{Hexane} Et_2NLi + BuH$$
 (1)

$$4 \operatorname{Et_2NLi} + \operatorname{ZrCl_4} \xrightarrow{\text{Toluene, THF}} \operatorname{Zr(NEt_2)_4} + 4 \operatorname{LiCl}$$
(2)

$$Zr(NEt_2)_4 + 4^tBuOH \xrightarrow{Toluene} Zr(O^tBu)_4 + 4 Et_2NH$$
 (3)

Both the compounds were purified by distillation under reduced pressure (Zr(NEt<sub>2</sub>)<sub>4</sub>: 80 °C/10<sup>-2</sup> Torr; Zr(O'Bu)<sub>4</sub>: 50 °C/10<sup>-2</sup> Torr). The NMR data ( $\delta$ , ppm) corresponds to their possible monomeric structures (1 and 3) in the solution (C<sub>6</sub>D<sub>6</sub>). **Zr(NEt<sub>2</sub>)<sub>4</sub>**: <sup>1</sup>H NMR: 1.12 *t* CH<sub>3</sub>; 3.32 *q*, CH<sub>2</sub>. <sup>13</sup>C NMR: 16.68, CH<sub>3</sub>; 43.04, CH<sub>2</sub>. **Zr(O'Bu)<sub>4</sub>**: <sup>1</sup>H NMR: 1.31 *s*, CH<sub>3</sub>. <sup>13</sup>C NMR: 32.47 CH<sub>3</sub>; 74.69 C(CH<sub>3</sub>)<sub>3</sub>.



## Chemical Vapor Deposition

The gas-phase decomposition of the metal-organic precursors was investigated on a cold-wall horizontal CVD reactor [20j] operating under reduced pressure. The Fe substrate rests in the quartz reactor on a graphite susceptor, which is heated inductively using a radio frequency generator. The temperatures were monitored using a thermocouple attached to the susceptor. The precursors (1:  $Zr(NEt_2)_4$ , 2: ( $Zr(NEt_2)_4 + HNEt_2$ ) and 3:  $Zr(OBu^t)_4$ ) were introduced in the reactor through a glass flange by applying dynamic vacuum (10<sup>-4</sup> to 10<sup>-6</sup> Torr) and maintaining the precursor reservoir at the appropriate temperature (50 °C for 1 and 40 °C for 2 and 3). The thermolysis products were removed through the pumping end of the reactor that was connected to rotary vane and turbo molecular vacuum pumps.

## Film Characterization

Surface morphology and elemental distribution in the films were recorded on a scanning electron microscope JSM-6400F (JEOL) coupled with an energy dispersive X-ray facility (EDX). The phase characterization and texture analysis was done by powder X-ray diffraction (XRD) analysis performed on a Siemens D-5000 diffractometer using Cu K $\alpha$  ( $\lambda = 1.54$  Å) radiation at room temperature. The XPS analysis was performed on a Surface Science Instrument SSI-M-Probe using Al K $\alpha$  radiation. The data were charge referenced to C 1s peak at a binding energy of 284 eV.

#### **Results and Discussion**

## Film Growth

The precursors,  $Zr(NEt_2)_4$  and  $Zr(OBu^t)_4$ , were chosen due to their high vapour pressures, gas phase stability and the presence of *pre-formed* Zr-O and Zr-N σ-bonds that should favour the formation of ZrO2 and ZrN solid-state phases at low processing temperatures. Moreover, the use of a single molecular source in the CVD process simplifies the growth parameters and allows a precise control over the phase, composition and particle size in the deposits [20]. In addition to neat amide precursor, a mixture of  $Zr(NEt_2)_4$  and Et<sub>2</sub>NH (1:1, w/w) was also employed in order to obtain nitrogen-rich deposits through a matrix assisted chemical vapor deposition (MA-CVD). The three precursor systems are denoted as  $Zr(NEt_2)_4$  (1),  $Zr(NEt_2)_4$  + HNEt<sub>2</sub> (2) and  $Zr(OBu^{t})_{4}$  (3), in the following text. The thermal decomposition of the precursor systems was investigated in a coldwall CVD reactor described in our earlier publications [20]. The films obtained from 1 and 2 showed blue, yellowish brown or gold colour depending upon the deposition temperature whereas the coatings produced using 3 were grey.

## **Phase Identification and Composition**

The X-ray diffraction profiles (Fig. 1) of films deposited using 1 and 2 on steel substrates showed broad peaks indicative of small particle size and/or poor crystallinity of the coatings in the temperature range 550-750 °C. The observed diffraction patterns correspond to the reported data for cubic zirconium carbonitride phase with highest intensity observed in our samples for the (111) peak [29]. The energy dispersive X-ray (EDX) analysis of the films obtained by the CVD of both 1 and 2 showed the presence of Zr, C, N and significant amount of O. The X-ray photoelectron spectra (Fig. 2) of the as-deposited film (from 1) showed the presence of Zr, C and O with a small amount of N. The elemental composition determined after Ar<sup>+</sup> sputtering performed to remove the oxidized surface, reveals higher nitrogen content in the film demonstrating the surface oxidation of the films. However, the films contained even after sputtering significant amount of oxygen, which indicates that the oxidation zone is larger in ZrN films deposited on steel [9, 14]. The presence of carbon even after several sputtering steps rules out its presence as organic residue and suggests the formation of a carbonitride phase (Zr-C-N) [30]. The similar values of lattice parameters for cubic ZrC (469 pm), ZrN (458 pm) and  $Zr(C_xN_y)$  (459 pm for x = y) phases prevent an unambiguous determination of stoichiometry and phase identification. Since the precursor did not possess Zr-C bonds, the formation of pure ZrC



Figure 1 XRD patterns (Cu K<sub> $\alpha$ </sub>) of Zr-C-N films obtained from 1 and 2 at 550 °C.



Figure 2 XPS overview spectra of Zr-C-N (derived from 1 and 2) and  $ZrO_2$  films (3) deposited at 550 °C.

phase is less probable, particularly in view of the rather low deposition temperatures. It is more likely that the presence of N-C units in the amide groups favours the formation of carbonitride composition as also suggested by the XRD and XPS studies (Figs. 1 and 2). This is confirmed by the observed chemical shift of C1s in the XPS spectra (285 eV) while the peak corresponding to the zirconium carbide phase is expected at  $\sim 282 \text{ eV}$  [6]. As expected, the ZrO<sub>2</sub> films contain only minor amount of residual carbon in the films (Fig. 2), which was found to be present mainly on the film surface.

Given the fact that the precursor is devoid of oxygen and the films were grown under low pressure conditions, the oxygen mainly originate from an *ex situ* surface oxidation of the film that is likely due to the weaker Zr-N bonds and the higher reactivity of nanostructured surface towards atmospheric oxygen. The replacement of nitrogen by oxygen or incorporation of additional oxygen is visible in the colour change from blue (as deposited) to brownish yellow (after 48 h). This stoichiometric variation influences the free electron concentration of the metal (Zr) that is responsible for the reflectivity and colour of nitride films [14]. It has been shown that the degree of oxidation is restricted to a few monolayers on Si substrates, whereas the oxidation zone is much deeper in the case of Fe substrates [9] as found in this study (vide supra). The higher affinity of zirconium towards oxygen is a well-known limitation in the fabrication of nitride films, and it has been demonstrated [31] that reactive sputtering of metallic zirconium in N<sub>2</sub>-O<sub>2</sub> atmosphere with a nitrogen content of 80 % produced pure films of monoclinic ZrO2. According to thermodynamic considerations, these observations are supported by the higher Gibbs free energy for  $ZrO_2$  (~ -1020 kJ/mol) when compared to ZrN ( $\sim -315$  kJ/mol) which makes ZrO<sub>2</sub> more stable under standard conditions.

The presence of an additional nitrogen source in 2 (in the form of free Et<sub>2</sub>NH) was employed to obtain N-rich films and to reduce the incorporation of carbon. As expected, the partial pressure of diethyl amine produced coatings with increased N content and reduced carbon percentage (Fig. 2). Further, the films deposited using  $Zr(NEt_2)_4 + Et_2NH$ precursor system were stable towards oxidation (no evident colour change) and showed visibly better reflectivity. However the X-ray diffractograms of the films deposited at 550, 650 and 750 °C exhibit patterns similar to those observed for films deposited using 1 as precursor, which shows that phase composition did not change significantly, and zirconium carbonitride composition is also present in the film obtained from 2. Although oxygen is evident in the XPS analysis, the formation of an oxide overlayer is not indicated in the X-ray diffraction patterns of the films. It is possible that the oxidized overlayer in the Zr-C-N films do not have a definite structure.

## Morphology and Microstructure

The Zr-C-N films obtained using 1 and 2 exhibited a granular morphology made up of spherical particles of nanometric dimensions. The deposition temperature did not show any remarkable change in the morphological features, in both cases. The high-resolution scanning electron micrographs (Fig. 3) of the Zr-C-N films show a smooth surface for the films obtained from 1, whereas a nanostructured surface is observed in the case of 2. In contrary to the Zr-C-N films, the ZrO<sub>2</sub> films exhibited characteristic morphology (Fig. 4) at different temperatures (350-650 °C). For instance, the film deposited at 450 °C shows a dense microstructure formed by cross-linked elongated grains (Fig. 4a). At higher deposition temperatures (550 and 650 °C), the grains exhibit a facetted morphology (Fig. 4b and c). The observed morphology change is also associated with a structural change as shown by the X-ray diffraction studies of these films (see later). The cross-sectional SEM



Figure 3 SEM images of Zr-C-N films deposited from (a) 1 and (b) 2.



Figure 4 (a-c) In-plane SEM images of  $ZrO_2$  obtained at 450, 550 and 650 °C. (d) Cross-sectional SEM image of a  $ZrO_2$  film on iron substrate (at 650 °C).

image (Fig. 4d) of a  $ZrO_2$  film (at 650°C) showed a dense and columnar microstructure.

The as-obtained  $ZrO_2$  deposits were crystalline in the temperature range 350-650 °C (Fig. 5). The X-ray diffraction pattern of the film deposited at 350 °C revealed a nanocrystalline deposit of tetragonal (*t*)  $ZrO_2$ . The average grain size calculated from the X-ray diffraction data (Scherrer Formula) was found to be 6 nm. At 450 °C, both monoclinic (*m*) and *t*-ZrO<sub>2</sub> phases coexist indicating a temperature dependent *t*-to-*m* phase transformation. At higher deposition temperatures (550 and 650 °C), the phase transition is complete and only monophasic *m*-ZrO<sub>2</sub> is obtained. Although tetragonal phase is a high temperature phase among the ZrO<sub>2</sub> phases (monoclininc: stable up to 1205 °C; tetragonal: 1205-2377 °C and cubic: 2377 to the melting point at 2710 °C), its preferred formation at 450 °C



Figure 5 XRD patterns (Cu  $K_{\alpha}$ ) of ZrO<sub>2</sub> films deposited at 350, 450, 550 and 650 °C.

can be due to the lower surface energy of nanocrystalline t-ZrO<sub>2.</sub> This was proposed by Garvie [32] who predicted that  $ZrO_2$  particles with a critical size (< 10 nm) can be stabilized in the tetragonal form whereas particles larger than the critical size would undergo t-to-m transformation. This has been recently confirmed by Chraska et al. [33] using a simple thermodynamic model that suggests that even larger grains could be stable as tetragonal if they directly nucleate in the tetragonal modification. The analysis of the XRD data of the CVD deposits obtained at higher temperatures (> 450 °C) suggests that  $ZrO_2$  nucleates on the substrate surface in the tetragonal phase but transforms gradually to monoclinic phase presumably due to increasing grain size. The primary nuclei formed in the CVD process rapidly grow through different phenomena such as coalescence and adsorption of new adatoms on the existing nuclei, which can be governed by the substrate temperature and gas phase supersaturation. The intensity of observed peaks and absence of other reflections in XRD patterns suggest a preferred growth orientation for the grains. This texture effect can be discerned from the scanning electron micrographs of the  $ZrO_2$  films (Fig. 4).

## Microhardness and Adhesion Test

The adhesion of the coatings was investigated using a diamond indenter (radius,  $2 \mu m$ ) that was pressed in the film with a given vertical load (F<sub>z</sub>) and moved on the surface in a horizontal direction. The vertical load was gradually increased to enhance the horizontal friction drag (F<sub>y</sub>) up to a critical load value (L<sub>c</sub>) where the coating will be removed. The L<sub>c</sub> values for the Zr-C-N films obtained at 550 °C from **1** (0.08 N) and **2** (0.1 N) suggest that the adhesion of films obtained from **2** is better than that obtained from **1**. The scanning electron micrographs (Fig. 6) of the scratch regions for the films obtained from **1**, **2** and **3** reveal that the films do not show characteristic spalling typically observed in ceramic films. Apparently, small amount of pyrolytic carbon is also present in the film that leads to an enhanced plasticity at the expense of hardness [34]. Indeed, the micro-



Figure 6 SEM images of scratch traces performed on Zr-C-N ((a) 1 and (b) 2) and (c)  $ZrO_2$  films.



Figure 7 Hardness of Zr-C-N (1 and 2) and  $ZrO_2$  films deposited at 550 °C.

hardness (H<sub>k</sub>) values for the Zr-C-N films (Fig. 7) obtained by the CVD of **2** at 550, 650 and 750 °C show a gradual decrease with H<sub>k</sub> values of 5.65, 3.68 and 2.11 GPa, respectively. It can be envisaged that higher deposition temperatures promotes the decomposition of amine molecules in the gas phase resulting in a higher incorporation of residual carbon in the films, which can lower the hardness values [34]. The H<sub>k</sub> value of 4.98 GPa in the films obtained by the CVD of **1** at 550 °C was lower than the hardness value in films deposited at same temperature using **2** as precursor. This lowering in H<sub>k</sub> value can be ascribed to the stronger oxidation of the films obtained from **1**. Further studies, re-

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quired to validate these findings, are currently underway. The  $H_k$  value of a  $ZrO_2$  film deposited at 550 °C was found to be 4.64 GPa (Fig. 7). The scratch test results on  $ZrO_2$  films deposited at 550 °C showed the films to be strongly adherent to the substrate ( $L_c = 0.1$  N).

# Conclusions

Zirconium carbonitride (Zr-C-N) and zirconium oxide  $(ZrO_2)$  films were deposited using  $Zr(NEt_2)_4$  and  $Zr(OBu^t)_4$ precursors, respectively in a low pressure cold wall CVD reactor. The Zr-C-N films obtained using pure Zr(NEt<sub>2</sub>)<sub>4</sub> easily oxidize under ambient conditions. The atmosphere oxidation is accompanied by a change in the colour of asdeposited films. The XPS analysis revealed a strong incorporation of oxygen at the surface, which is associated with lowering of nitrogen content in the surface layers. A decreasing oxygen concentration is observed away from the film surface but still significant amount of oxygen was found in the film bulk. In order to obtain N-rich films, Zr(NEt<sub>2</sub>)<sub>4</sub> was mixed with Et<sub>2</sub>NH and used in the CVD process. The bronze-coloured films obtained from this precursor system showed a better colour stability and a lower oxygen content, although the overall phase composition and morphology did not show any considerable change.

The phase composition and morphology of zirconium dioxide films showed a marked dependence on the deposition temperatures (450-650 °C) whereas the precursor flux influenced the growth rates. The films obtained at 350 °C were purely tetragonal  $ZrO_2$  (<d> 6 nm) whereas coexistence of tetragonal and monoclinic phases was observed at 450 °C (<d> 16 nm). The formation of *t*-ZrO<sub>2</sub> at lower temperatures is possibly a surface energy effect that favours the formation of *t*-ZrO<sub>2</sub> nuclei below a critical particle size (10 nm) beyond which transformation to monoclinic phase occurs. This was supported by the XRD analysis of films deposited at 550 and 650 °C, which revealed monophasic *m*-ZrO<sub>2</sub> with average particle sizes of 34 and 40 nm, respectively.

This study shows that the composition, microstructure and properties of CVD coatings are a function of both deposition condition and the molecular level chemistry involved in the precursor decomposition. The deficiency of nitrogen in the films obtained from the CVD of Zr(NEt<sub>2</sub>)<sub>4</sub> can be due to the labile Zr-N bond in the precursor and its premature cleavage in the gas phase. To circumvent a thermally induced scission of metal-ligand unit present in the molecular precursor, an excess of free ligand (Et<sub>2</sub>NH) was used to provide a partial pressure of N-containing species in the deposition zone. This approach resulted in a slightly increased nitrogen content in the film and simultaneously improved the colour stability and adhesion of the Zr-C-N coatings. In contrast to the above, the extraordinary stability of Zr-O bonds in Zr(OBu<sup>t</sup>)<sub>4</sub> results in a clean conversion of the molecular source to the solid-state phase.

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