

NANOSTRUCTURED FUNCTIONAL CERAMIC COATINGS BY MOLECULE-BASED CHEMICAL VAPOR DEPOSITION

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Abstract. Thin film deposition by chemical vapor deposition (CVD) techniques plays a dominant role in the development of both protective and functional coatings, important for their technological implications. Commonly, multi-component materials are prepared from a mixture of precursors, however the efficiency of such processes is hampered by the mis-match of chemical reactivity such as differential thermal stability and vapor pressure of individual precursor species. Consequently, phase separation and elemental segregation are usually observed in coatings produced by CVD. De-mixing of elements in multi-component systems is thermodynamically driven and sensitive to the chemical behavior of the precursors. Transformation of precursor compounds possessing bonding features inherent to the solid-state lowers the need of diffusion and counter-balances the thermodynamic impediments. We discuss here the role of pre-defined chemical precursors in reducing the constraints imposed on conventional CVD techniques, which require rather high deposition temperatures and generally offer marginal control over microstructure and surface topography. Examples dealing with the decomposition of molecular sources in CVD process to deposit gas sensing, photocatalytic and bio-compatible coatings are also presented.

1. INTRODUCTION

Development of nanostructured ceramic coatings has become an important research area mainly due to the interesting chemical and physical properties of nanoscaled materials [1-11]. Chemical vapor deposition (CVD) is a versatile technique for low-temperature deposition of functional ceramics with attractive process features such as up-scaling to large scale production, conformal coverage, and easy regulation of deposition parameters. In molecule-based CVD techniques, the deposition process operate at atomic or molecular level, which opens up the possibility of obtaining dense microstructure and thus allow to achieve the beneficial properties of monolithic ceramics (high thermal,

mechanical and chemical resistance) in form of protective and functional coatings. In addition, application of well-defined molecules as precursor units offers precise control over structure, morphology and composition of resulting coatings either through influence of chemical design or by the variation of process parameters [12-14].

The **molecule-to-material** concept denotes the transformation of the intrinsic chemical configuration of molecular precursors, under non-equilibrium conditions, into solid phases at much lower temperatures than those required for conventional ceramic processing procedures [12]. One of the basic requirements for thin film growth is that the precursor units adsorb on the substrate only at spe-

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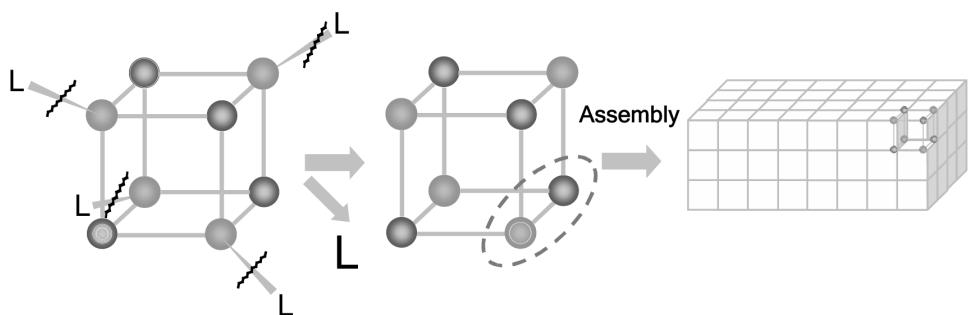


Fig. 1. Conceptual representation of molecule-to-material transformation.

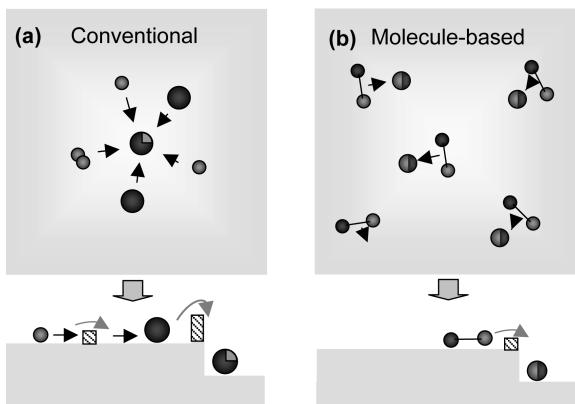


Fig. 2. Qualitative representation of energy barriers in (a) conventional and (b) molecule-based CVD processes.

cific sites, for instance, attachment of ad-species on an activated free site against adsorption and diffusion on top of a growing island, a situation generally caused due to lattice and thermal conductively mismatch among substrate and growing material. Chemical codes in the metal-organic precursor enable controlled surface diffusion due to pre-formed metal-ligand units. The stability of M-L linkages (M: metal; L: anion) together with similarity of elemental stoichiometry towards target solid-state phases are useful in lowering the activation energy barrier for the nucleation process (Fig. 1) [12].

Film growth in multi- and single-source approaches differs in terms of energy barriers related to surface reactions and diffusion of ad-atoms (Fig. 2). Compared to the conventional CVD process, in which the movement of ad-atoms is thermodynamically controlled, surface-controlled diffusion in molecule-based CVD is favored by structural and chemical relevance of precursor units to the film materials. We report herein, synthesis of nanostructured oxide films by CVD followed by

evaluation of their functional properties. We also discuss the role played by precursor chemistry in the growth of film material.

2. RESULTS AND DISCUSSION

The following text presents selected examples to elucidate the role of precursor design and processing parameters in the growth of nanostructured functional films with controllable properties.

2.1. Surfaces for gas sensing

Tin oxide is a wide band gap ($E_g \sim 3.6$ eV) semiconducting material which plays an important role in the development of resistive-type gas sensors [15,16]. CVD of a single molecular source, $[\text{Sn}(\text{OBu}')_4]$, with pre-existent Sn-O units, successfully produced tin oxide nanostructures with controllable morphologies as shown in Fig. 3. The observed distinct morphologies of tin oxide surfaces can be caused by several competing factors such

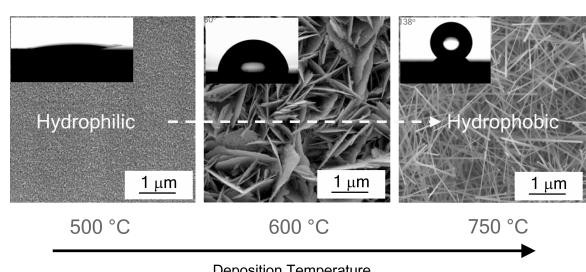


Fig. 3. SEM images of SnO_2 nanostructures deposited at 500, 600, and 750 °C. Contact angle of water droplet on different morphologies is shown in inset.

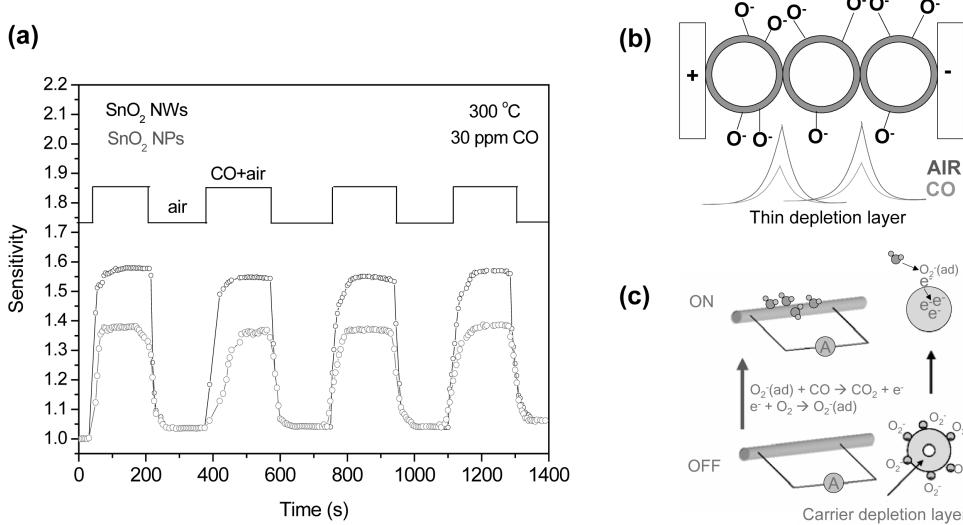


Fig. 4. (a) Gas sensing behaviors of SnO_2 nanoparticles and nanowires and (b-c) the corresponding sensing mechanisms.

as sticking coefficient, surface diffusion, and energy/flux distribution of the intermediate species and their interaction with the substrate, which all play a role in the evolution of surface roughness. The films were deposited under similar precursor flux with substrate maintained at different temperatures. Films deposited at 500 °C showed a granular morphology constituted by nano-sized particles of regular shape, which can be attributed to an island-type growth due to film-substrate mismatch and the low mobility of grain boundaries at growth temperatures. Upon increasing the temperature, development of texture effects was observed (Fig. 3) probably due to the difference in the growth rates between several crystal planes at the surface of the film [17]. Crystallites oriented with their slower growing direction normal to the surface are terminated while faster growing directions are preserved as they intersect the grain boundary. As a result, the obtained films are strongly faceted, generally exhibiting faces corresponding to low index crystallographic planes. The growth rate of the different facets may depend on several factors, including their inclination relative to the precursor flux, sticking coefficients, site specific reaction rates, etc. This mechanism leads to preferential deposition/growth of atoms at low-energy surfaces in order to minimise the surface energy as revealed in the growth of one-dimensional nanostructures (Fig. 3). These results are interesting because microstruc-

ture and surface topography are critical parameters for the performance of metal-oxide gas sensors [18]. Whereas smaller grain size can produce high surface-to-volume ratios which can enhance sensitivity, one or two-dimensional single crystal films have the advantage of faster response as the effects of grain boundary diffusion of the detected gas and losses due to charge carrier scattering are reduced. Controlled modulation of surface microstructure is desirable to be able to control the gas sensing properties of ceramic coatings. Comparative evaluation of the gas sensitivity of films composed of nano-grains and nanowires towards carbon monoxide (CO) revealed an enhanced gas sensing performance (Fig. 4) for nanowire sample. The higher sensitivity is possibly due to increased and selective adsorption of CO molecules on the crystalline facets of nanowire structures, higher charge penetration and reduced charge percolation effects expected in a one dimensional structures, when compared to granular film [19-21].

2.2. Photocatalytic coatings

Anatase and rutile modifications of titanium dioxide (TiO_2) exhibit different photo-chemical behavior due to different bandgap values (anatase: 3.18 eV → rutile: 3.03 eV) [22,23]. Given the facile anatase to rutile phase transition, films processed by conventional processing techniques show coexist-

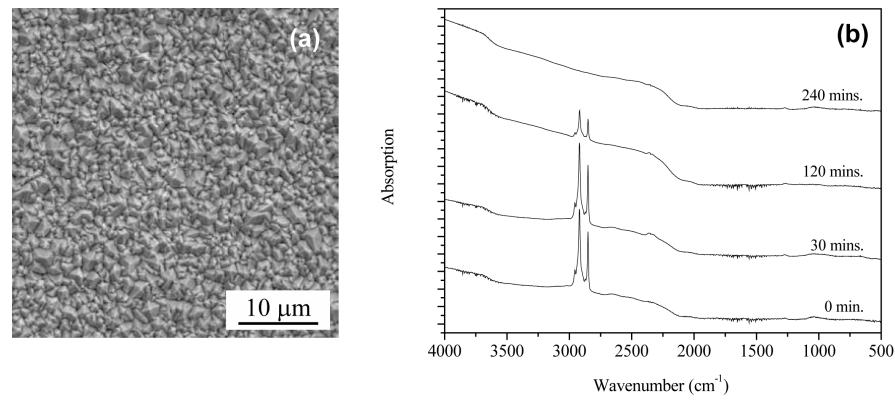


Fig. 5. (a) SEM images of TiO_2 coating on glass at $550\text{ }^\circ\text{C}$ and (b) FT-IR spectra of stearic acid coated TiO_2 recorded following UV irradiation after different time periods.

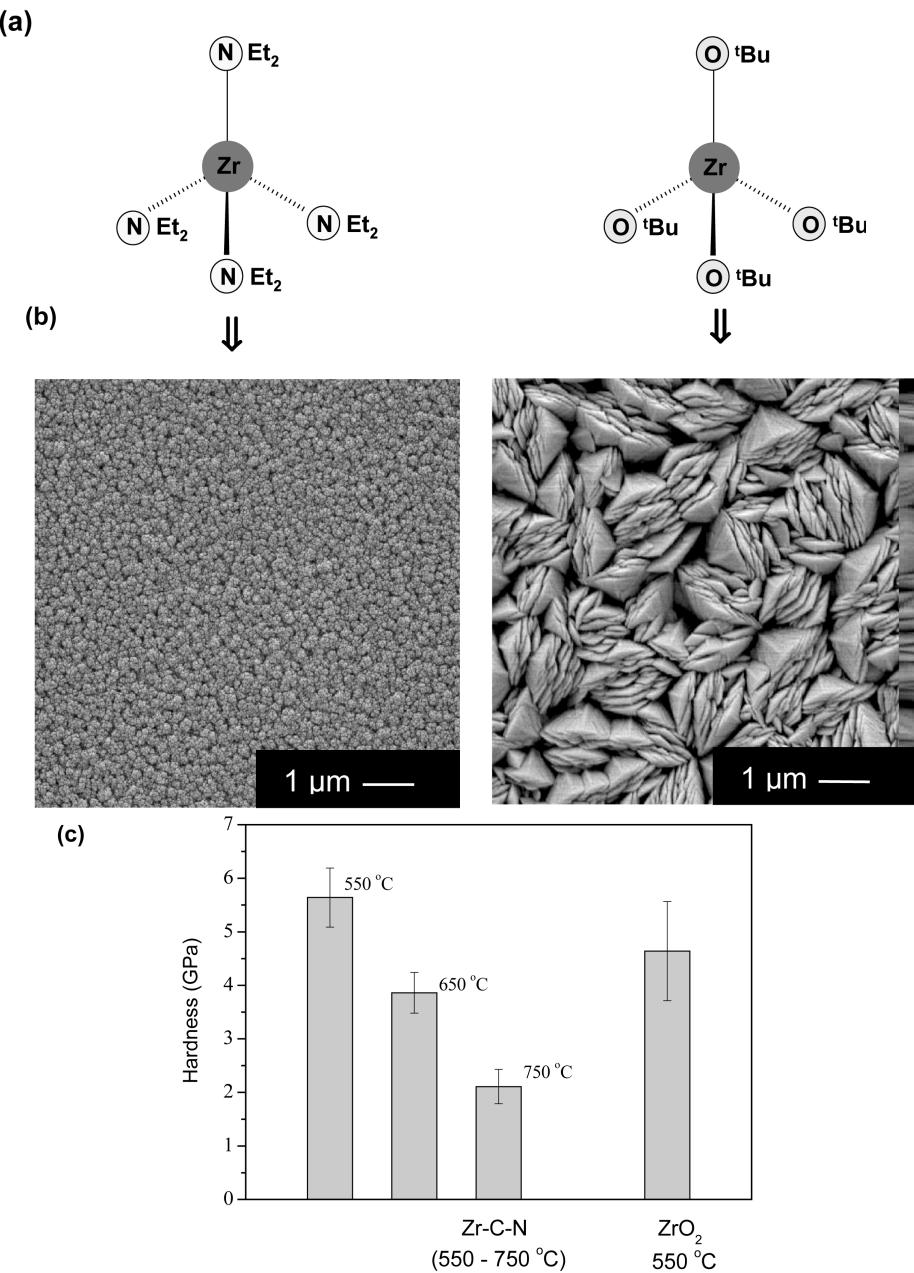


Fig. 6. (a) Chemical structures of $\text{Zr}(\text{NEt}_2)_4$ and $\text{Zr}(\text{O}^t\text{Bu})_4$ molecules and (b) SEM images of Zr-C-N and ZrO_2 coatings. (c) Hardness measurement of Zr-C-N and ZrO_2 films.

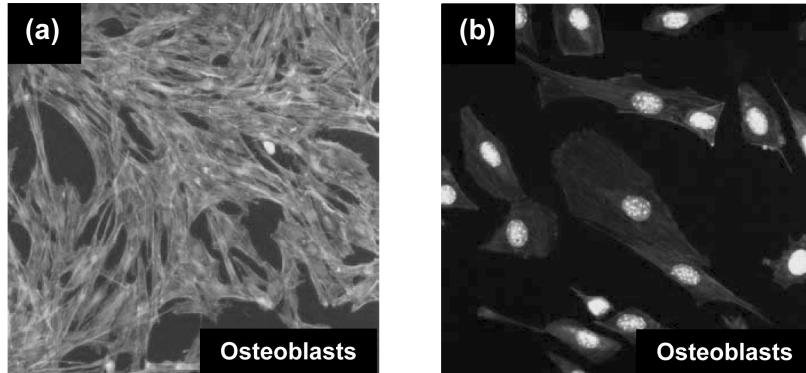


Fig. 7. Cell growth and adhesion behaviors of osteoblasts on (a) ZrO_2 and (b) Zr-C-N surfaces.

ence of rutile and anatase phases in the most cases [24,25]. The low process temperatures in molecule-based CVD techniques allow kinetically controlled deposition of metastable phases such as anatase. The CVD of $[\text{Ti}(\text{O}^{\prime}\text{Pr})_4]$ at 550 °C produced monophasic anatase deposits, which could be discerned from the typical faceted morphology of the grains as observed in scanning electron microscopy (SEM) images (Fig. 5a) and proven by the X-ray diffraction (XRD) data. To investigate the photocatalytic property of TiO_2 film, a thin film of stearic acid (10 mM) was deposited on TiO_2 surface by spin-coating techniques followed by illumination with a UV lamp (365 nm, 10 mW). The stearic acid on the TiO_2 surface decomposed to CO_2 and H_2O after the UV irradiation [26].



To verify the degradation process, infrared spectra of the films were recorded in regular time intervals (Fig. 5b), which showed that stearic acid began to degrade in 30 minutes of UV irradiation and was completely decomposed in 240 minutes. The photochemical conversion was probed by the intensity of C-H bond vibrations (2960, 2920 and 2850 cm^{-1}) of stearic acid in the infrared spectra (Fig. 5b). When compared to the literature reports [27], the photo-activity of the CVD films were found to be higher presumably due to the presence of pure anatase phase in our samples and enlarged surface area due to nano-topography of the films.

2.3. Biocompatible coatings

In this section we compare the biocompatibility of zirconium oxide and carbonitride films deposited

by CVD of $\text{Zr(O}^{\prime}\text{Bu})_4$ and $\text{Zr(NEt}_2)_4$ [28] containing Zr-O and Zr-N-C units, respectively. In comparison to smooth surface morphology of Zr-C-N film, ZrO_2 films displayed a textured surface with developed crystalline facets of individual grains (Fig. 6). Monoclinic and tetragonal ZrO_2 phases co-exist in films deposited at 450 °C, whereas pure monoclinic deposits were obtained at higher temperatures (> 450 °C). The amorphous Zr-C-N films deposited at 550 °C show higher hardness values than those of crystalline ZrO_2 samples indicating the role of substrate temperature and associated sintering effects. However, the hardness of Zr-C-N samples was found to decrease with increasing substrate temperature. It can be envisaged that higher deposition temperatures promote the decomposition of amide ligands in the gas phase resulting in a higher incorporation of residual carbon in the films, which can lower the hardness values.

Given the chemically inert nature of ZrO_2 and Zr-C-N films, we have investigated the biocompatibility of these surfaces by cultivating osteoblasts on these surfaces. Fig. 7 shows the growth behavior of cells on zirconium oxide- and carbonitride samples; osteoblasts on ZrO_2 films display homogeneous and dense cell population due to a fast and pronounced cell growth (Fig. 7a). When compared to ZrO_2 films, slower growth rates were observed on Zr-C-N coatings, although cell growth behavior was also observed in this case. Apparently, the granularity and porosity of ZrO_2 films support the cell growth. These results indicate that nanostructured biocompatible surfaces can help to interface living cells, for instance by reducing time required for adherence, which may find applications in developing coatings for implants. In addi-

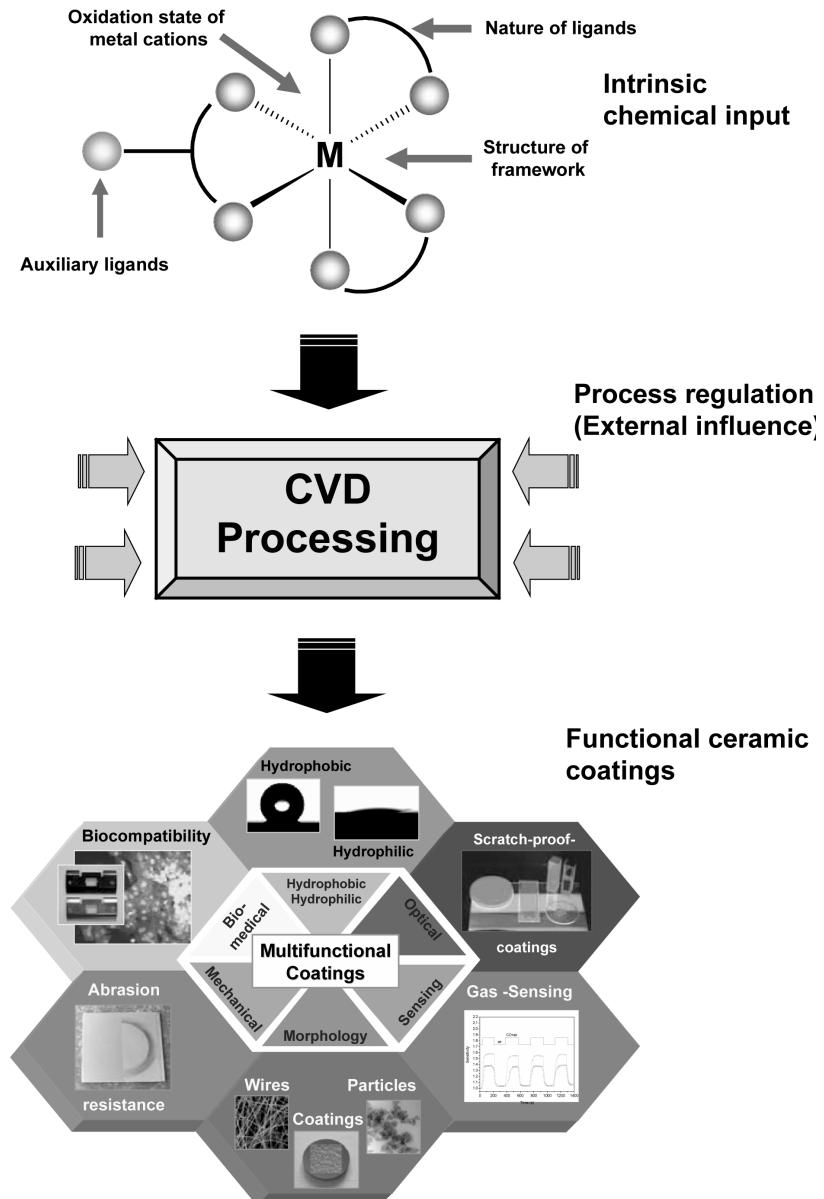


Fig. 8. The influence of chemical codes of precursors in controlling the CVD process and the resulting functional properties of ceramic coatings.

tion, it opens possibilities for modulating fundamental cell behaviors (proliferation, adhesion, migration and differentiation) by tuning the physical surface features.

3. CONCLUSIONS

Ceramic coatings are essential to improve the performance and extend the lifetime of the device

parts. The potential and versatility of the conventional high temperature CVD process can be substantially enhanced by applying precursor-design concept, which not only reduces the processing temperature but also offers better film-substrate adhesion and facile microstructure control. The gas phase decomposition of molecular sources with defined metal-ligand bonding is an interesting alternative to conventional multi-source approaches

because the composition, microstructure, surface properties of films can be programmed by precursor design in the synthetic stage and further tuned during the stage of CVD processing by adjusting the deposition parameters. Fig. 8 shows the intrinsic and extrinsic influences of molecular precursors on the fabrication of nanostructured coatings with controlled structure, morphology and functional properties. Most of the solutions and applications indicated in Fig. 8 are a function of the inherent properties of the bulk material and unique features arising due to nanoscopic grain sizes (quantum effects, surface area and surface energy).

The nanoparticle-nanoflake-nanowire morphology transition of SnO_2 is probably related to surface energy and different growth rates along different crystal directions. The temperature dependent diffusion rate and length play a key role in the structure reorganization in order to minimize the surface energy. The surface properties of SnO_2 such as hydrophilic \rightarrow hydrophobic transition can depend not only on the variation of morphology, but also on the induced changes of surface chemistry such as presence of defects, internal strains and modified surface structures. The surface effect of nanostructured films can be also observed in the investigation of photocatalytic behavior of anatase TiO_2 nanostructures. The metastable anatase with nano-topography can be obtained by kinetically suppressing the grain growth of rutile phase at low deposition temperatures therefore enhancing the photocatalytic performance of TiO_2 films. Ceramic coatings with tunable and multifunctional properties can be achieved by optimization of precursor design and processing parameters. For instance, zirconium oxide and carbonitride films can be easily deposited by variation of precursor configurations and heat-treatment resulting in better adhesion, mechanical hardness and biocompatibility. The controlled formation of functional ceramic coatings promises applications in the area of nanoelectronics, gas sensors, photocatalysts and bio-technologies.

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