

# Characterization of core/shell nanoparticle thin films for gas analytical applications<sup>†</sup>

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Gas analytical microsystems such as the Karlsruhe micro nose (KAMINA) can be improved toward higher sensitivity when using SnO<sub>2</sub> nanoparticle thin films instead of well-established sputtered layers. For achieving long-term stability, such nanoparticles must be prevented from growing and agglomerating. A very promising approach is to coat SnO<sub>2</sub> nanoparticles with an open-pored SiO<sub>2</sub> shell, simply acting as a spacer, while preserving electrical contact between adjacent core particles. Such nanoparticulate thin films can easily be realized by the gas-phase Karlsruhe microwave plasma process (KMPP). This provides an all-in-one approach to synthesize particles with diameters less than 10 nm, to coat them *in situ* with a protective ultrathin SiO<sub>2</sub> shell in a downstream step and to finally deposit the core/shell particles solvent-free onto prefabricated micro devices.

The present study focuses on the surface analytical characterization of 200 nm thin films consisting of SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticles with various shell designs. For this purpose, the SiO<sub>2</sub> shell thickness was systematically increased while keeping the SnO<sub>2</sub> core size constant. X-ray photoelectron spectroscopy (XPS) provides information concerning chemical binding states and shell thickness in a nondestructive manner. Angle-resolved XPS together with transmission electron microscopy (TEM) validate the achieved core/shell structure. In the case of the desired ultrathin SiO<sub>2</sub> shells, low-energy ion scattering (LEIS) is solely the suitable means to prove that Sn and Si are the constituents of the outermost monolayer of the spherical particles and it demonstrates the attainability of open-pored coatings. Copyright © 2010 John Wiley & Sons, Ltd.

**Keywords:** core/shell nanoparticles; nanoparticle films; silicon dioxide; stannic oxide; tin dioxide; gas sensors; XPS; LEIS; SEM; TEM

## Introduction

Sputtered SnO<sub>2</sub> thin films are well established as gas sensing layers in analytical microsystems such as the Karlsruhe micro nose (KAMINA).<sup>[1]</sup> To improve the performance toward higher sensitivity, a very promising approach is to replace the sputtered thin films with films made of SnO<sub>2</sub> nanoparticles. It has recently been shown that microarrays equipped with pure nanocrystalline SnO<sub>2</sub> achieve an increase in sensitivity of more than 1 order of magnitude.<sup>[2]</sup> However, these crystallites undergo significant grain growth at operating temperature (300–350 °C) and thus the efficiency of the material is lost.

The method known as Zener pinning involves restricting growth with temperature by addition of tiny discrete particles in the interface regions between the nanocrystals.<sup>[3–5]</sup> In contrast, our approach is to coat SnO<sub>2</sub> nanoparticles with a protective ultrathin SiO<sub>2</sub> shell. This can easily be achieved by the Karlsruhe microwave plasma process (KMPP), a versatile gas-phase plasma process suited to synthesize nanoscaled particles with diameters less than 10 nm and to coat them *in situ* in a downstream step.<sup>[2,6]</sup> Moreover, the final core/shell nanoparticles can be directly and solvent-free deposited onto prefabricated microdevices. These core/shell nanoparticles are expected to prevent the gas-sensitive cores from growing and agglomerating while maintaining the electrical conductivity. Therefore, a prerequisite is to achieve an open-pored SiO<sub>2</sub> shell enabling direct contact between adjacent SnO<sub>2</sub> nanoparticles, i.e. simply acting as a spacer.

In this contribution, we focus on the surface analytical characterization of such nanoparticle thin films with a thickness of 200 nm made of SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticles. In particular, X-ray photoelectron spectroscopy (XPS) reveals chemical binding

states and information on the shell thickness in a nondestructive manner. For this purpose, the SiO<sub>2</sub> shell thickness was systematically increased while keeping the SnO<sub>2</sub> core size constant. In the case of the desired open-pored ultrathin SiO<sub>2</sub> shells, low-energy ion scattering (LEIS) is solely the suitable means to distinguish between Sn and Si as constituents of the outermost monolayer of the spherical particles to prove the attainability of required open-pored coatings.<sup>[7]</sup> In addition, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to achieve a comprehensive characterization.

## Experimental

### Synthesis

The KMPP was used to synthesize SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticles with constant core size and different shell thicknesses. A detailed description of KMPP is given elsewhere.<sup>[2,6]</sup>

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Tin-IV-chloride (Sigma-Aldrich Chemie GmbH, München, Germany) was selected as the precursor material for the SnO<sub>2</sub> core particles. Different SiO<sub>2</sub> shell thicknesses were realized using silicon-IV-chloride (Riedel de Haen, Seelze, Germany) with varying feed rates. The process gases were in all cases an argon/oxygen 80/20 mixture (Ar 5.0, O<sub>2</sub> 4.8) as the reaction gas and argon (Ar 6.0) as the carrier gas for the evaporated precursors (basi Schöberl GmbH & Co. KG, Rastatt, Germany).

The substrates used for the nanoparticle film characterization were polished single crystal <100> silicon sections (10 × 10 × 0.35 mm<sup>3</sup>). For gas analytical tests, core/shell nanoparticle films were directly and solvent-free deposited onto basic structures of gas sensor microarrays,<sup>[2]</sup> which are currently composed of 38 sensor elements on an area of 4 × 8 mm<sup>2</sup>, and were manufactured by RF magnetron sputtering, applying a shadow masking technique.<sup>[8]</sup>

### Characterization

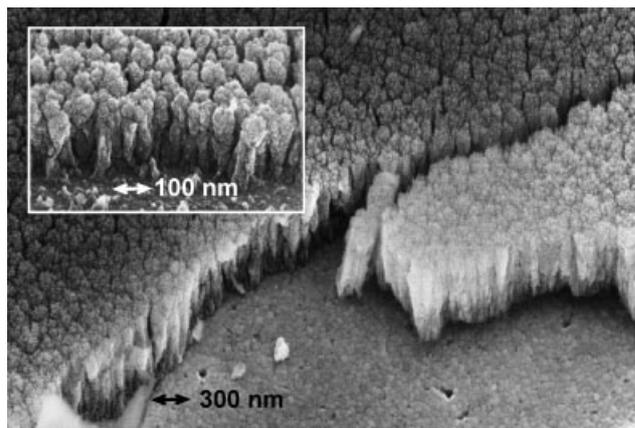
XPS measurements were performed using a K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.<sup>[9]</sup> All nanoparticle thin films were analyzed using a microfocused, monochromated Al K $\alpha$  X-ray source (30–400  $\mu$ m spot size). Angle-resolved spectra were obtained by acquiring six angles between 0° and 60° electron emission using the K-Alpha tilt stage. The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy, and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles [binding energy (BE) uncertainty:  $\pm 0.2$  eV], and Scofield sensitivity factors were applied for quantification.<sup>[10]</sup> All spectra were referenced to the C1s peak, assumed to originate from surface hydrocarbon contamination at 285.0 eV BE controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au.

LEIS measurements were taken using a Qtac<sup>100</sup> spectrometer (ION-TOF GmbH, Münster, Germany). In order to remove hydrocarbon contamination, all samples were cleaned using the atomic oxygen treatment for 40 min at sample temperatures up to 200 °C. LEIS spectra were obtained using 3 keV <sup>4</sup>He<sup>+</sup> scattering. Assuming a sputter yield of 0.1 atoms per He-ion at 6 nA target current,  $3.2 \times 10^{13}$  cm<sup>-2</sup> atoms were sputtered from the sample surface during the analysis.

SEM investigations were performed on a Zeiss Supra 55 scanning electron microscope (Carl Zeiss SMT AG, Oberkochen, Germany) using magnification up to  $3 \times 10^5$  at 15 kV accelerating voltage. TEM investigations were performed on a Tecnai F20-ST (FEI Company, Hillsboro, OR USA), operating at 200 keV. For TEM sample preparation, nanoparticles were deposited on 300 mesh Cu grids covered with holey carbon films. Gas analytical tests were performed with an ARTINOS electronic nose (SYSCA AG, Knittlingen, Germany) using 2-propanol in synthetic air at 50% relative humidity.

### Results and Discussion

Recently we have demonstrated a significant increase in gas analytical performance when replacing conventionally sputtered SnO<sub>2</sub> with bare SnO<sub>2</sub> nanoparticles synthesized by KMPP.<sup>[2]</sup> To counteract the drawback of poor long-term stability due to particle growth at 300 °C operating temperature, the promising approach



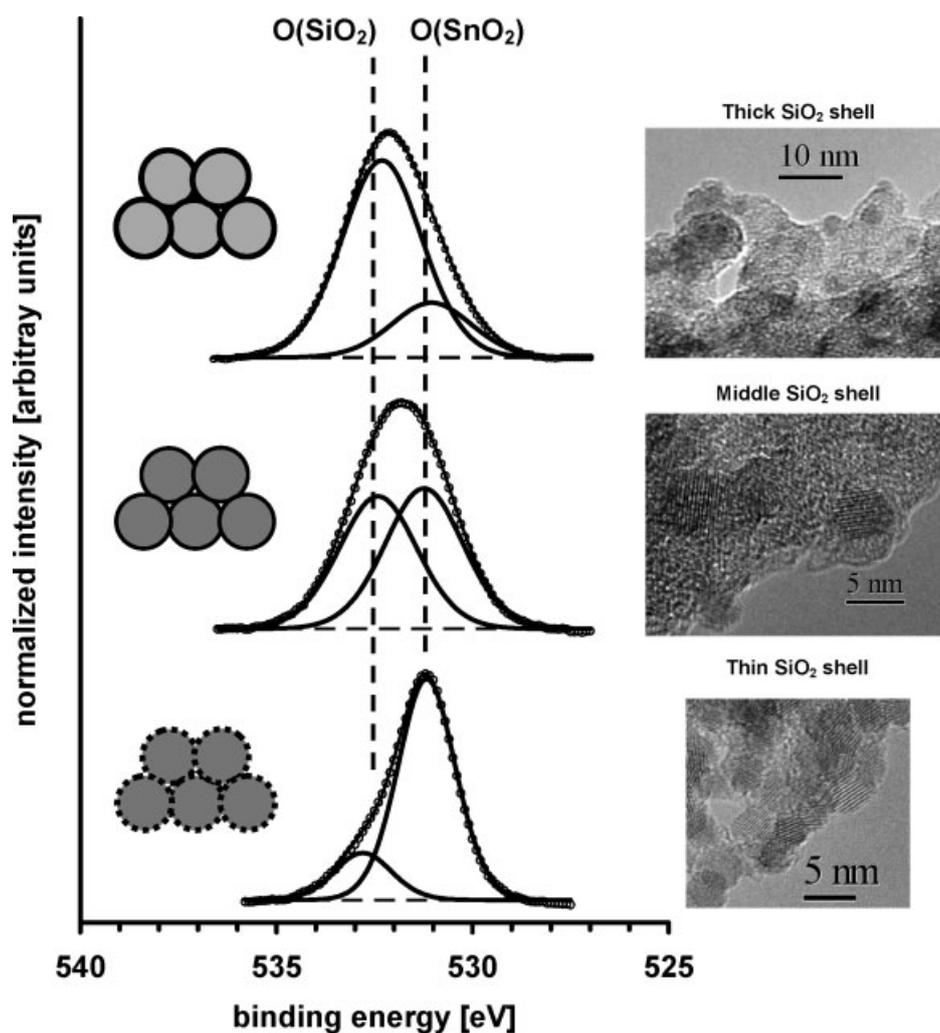
**Figure 1.** SEM images of a SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticle thin film, deposited directly and solvent-free onto a silicon substrate.

is to cover the functional SnO<sub>2</sub> particle with an inert open-pored SiO<sub>2</sub> spacer. A prerequisite for the core/shell particle development is its comprehensive surface analytical characterization. For this purpose, the SiO<sub>2</sub> shell thickness was systematically increased while keeping the SnO<sub>2</sub> core size constant. KMPP enables us to deposit nanoparticle films directly and solvent-free onto various substrates. The SEM images in Fig. 1 show the achievement of a closed primary layer growing up to a columnar film structure of about 200 nm thickness. As already known from previous bare particle characterization by means of TEM and electron diffraction,<sup>[2]</sup> the SnO<sub>2</sub> core particles crystallize in cassiterite structure and can be adjusted to a size of 4–5 nm with a narrow particle size distribution. The presence of the ultrathin SiO<sub>2</sub> shell cannot be well proven by TEM investigations, as its thickness is below the resolution limit of the microscope. Additionally, SiO<sub>2</sub> remains amorphous and provides only low elemental contrast on the amorphous carbon film. The open-pored structure of the shell therefore cannot be demonstrated by TEM. This is shown in Fig. 2, right part. The upper image shows SnO<sub>2</sub> nanoparticles coated with a thick SiO<sub>2</sub> shell. Here, one has the impression that SnO<sub>2</sub> nanoparticles (dark dots) are surrounded by an amorphous matrix. The middle image reveals particles with shell, but the cores are not well separated. In the lowest image, an open-pored shell is not visible. Hence, this is subject to verification by means of XPS and LEIS.

Therefore, XPS measurements were taken in order to obtain information on chemical binding states of the core/shell nanoparticle films and to estimate the SiO<sub>2</sub> shell thickness. The binding energies measured for SnO<sub>2</sub> (Sn 3d<sub>5/2</sub> = 487.3 eV, O 1s = 531.4 eV), and SiO<sub>2</sub> (Si 2p = 102.9 eV and O 1s = 532.3 eV), as well as for organic contaminants, are in a good agreement with reference data and are close to those reported in the literature.<sup>[8,11]</sup>

Angle-resolved XPS data justify the achievement of spherical core/shell nanoparticles as the expected identical Sn/Si intensity ratio was found for all applied electron emission angles, which is a direct verification of the core/shell structure.<sup>[12]</sup>

Additionally, XPS is suited to measure the thickness of nanoscaled thin films. The description of the detailed underlying formalism based on a modified Lambert–Beer equation and least square fitting recently has been the subject of a series of comprehensive studies.<sup>[8,9,13,14]</sup> In the case of Al (15 nm) core/Al shell nanoparticles, Sánchez-López and Fernández<sup>[15]</sup> proved that an assumed cubic shape for the particles, although not in close



**Figure 2.** O 1s XPS spectra of SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticle thin films with different shell thicknesses (left side) compared to representative TEM images (right side). For better visualization, the XPS spectra are normalized to maximum intensity.

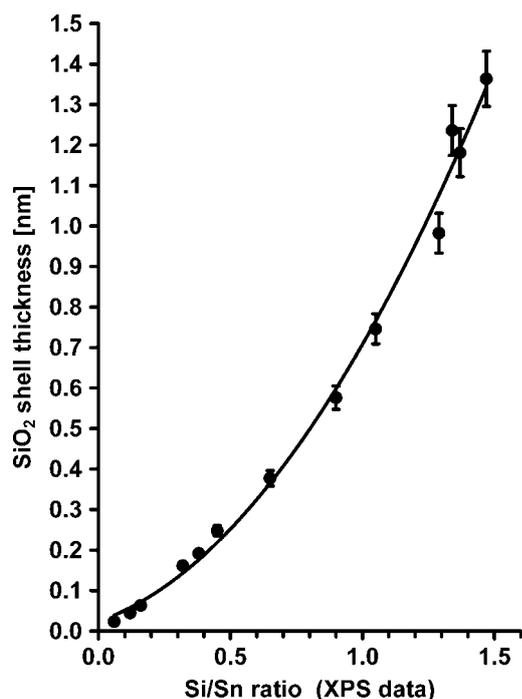
accordance to the observed morphology, is a reasonable model for quantitative XPS analysis for these samples. Therefore, the reported formalism was applied on the present SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticle films using Si 2p as the shell signal and Sn 3d<sub>5/2</sub> as the core signal, and considering that the XPS information depth covers nearly the complete particle (Fig.2). Together with TEM results of the uncoated SnO<sub>2</sub> nanoparticles, which reveal sizes of 4–5 nm for the SnO<sub>2</sub> core particles, the calculated SiO<sub>2</sub> shell thickness from the XPS measurements was found to be in the range 0.05–1.5 nm with a codependency on the precursor feed rate during synthesis (*cf* Fig. 3).

However, measurements and theoretical predictions of attenuation lengths may have large uncertainties (>6%) and published values vary by a factor of 2.<sup>[16,17]</sup> Together with experimental uncertainties, one can expect an entire deviation of about 20%. In spite of taking this into account, the XPS results are consistent with the restricted depth range of about 5 nm.<sup>[18,19]</sup> Organic contaminants were neglected because SiO<sub>2</sub> shell thickness calculations using O1s electrons of both oxides reveal the same results within the experimental uncertainty. Additionally, this is justified by LEIS results revealing a maximum adventitious carbon layer of less than 0.4 nm thickness for the bare SnO<sub>2</sub> particles calculated from the Sn onset peak shift during atomic oxygen cleaning.

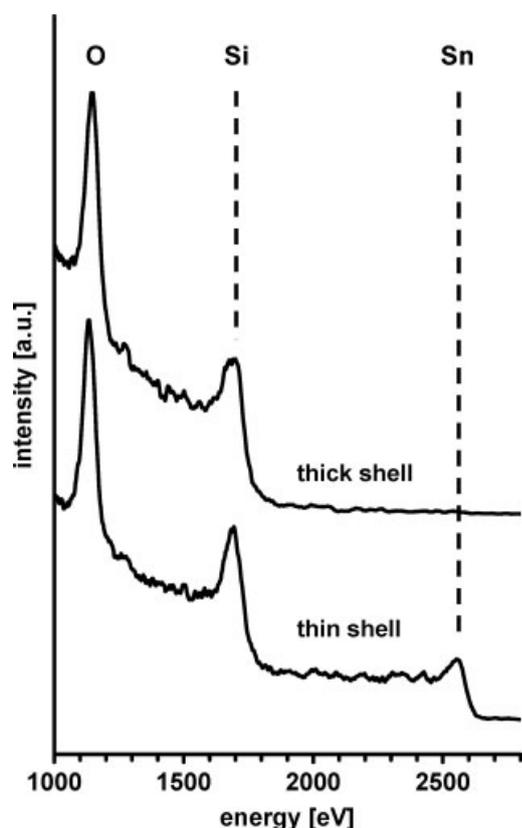
XPS findings alone give reason to assume an open-pored shell in the case of ultrathin coatings when considering the O<sup>2-</sup> ionic radius of 0.126 nm. The crucial proof, however, succeeded with LEIS measurements and is based on the appearance of their high-energy onset peaks which verify both Sn (2675 eV) and Si (1776 eV) to be constituents of the outermost monolayer of the spherical particles, as shown in Fig. 4.<sup>[7]</sup>

In the first attempt, pulsed gas exposure experiments on open-pored SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticle films demonstrate an overall improvement of the gas analytical properties compared to sputtered SnO<sub>2</sub> thin films and till now reveal long-term stability for more than 3 months. In particular, the dynamic range of the array is increased by a factor of 10 indicating a significant improvement in sensitivity. The response time remains similar to that of sputtered SnO<sub>2</sub> which obviously is due to the open-pored and columnar structure of the nanoparticle films (*cf* Fig. 1). However, the recovery time is slightly increased by a factor of 1.5 based conditionally upon the increase of the effective surface area.

Nevertheless, further shell optimization is necessary for the extension of lifetime while preserving the excellent gas sensing properties. In particular, the long-term behavior at elevated temperatures is currently under investigation.



**Figure 3.** SiO<sub>2</sub> shell thickness dependency on Si/Sn concentration ratios calculated from XPS data (bars indicate  $\pm 5\%$  error).



**Figure 4.** LEIS spectra of SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticle thin films with different shell thicknesses after atomic oxygen cleaning.

## Conclusions

Novel SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticle films for gas analytical application are attainable using the KMPP. Independent tech-

niques such as SEM and TEM, XPS, and LEIS must be combined for a comprehensive particle and film characterization. Herewith the SnO<sub>2</sub> core size, the achieved SiO<sub>2</sub> shell, and the respective chemical composition could be substantiated. The achievement of homogenous and crack-free films with columnar morphology of about 200 nm thickness was proved by SEM analysis. Finally, the desired open-pored ultrathin spacer shell, necessary for restricting the growth of the functional SnO<sub>2</sub> particles at elevated temperatures and to ensure electrical contact, was verified by LEIS measurements.

In addition, first gas analytical tests proved the significant increase of the sensor performance when replacing conventionally sputtered SnO<sub>2</sub> with SnO<sub>2</sub> core/SiO<sub>2</sub> shell nanoparticle thin films.

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## References

- [1] J. Goschnick, *Microelectron. Eng.* **2001**, *57*, 693.
- [2] B. Schumacher, R. Ochs, H. Troeße, S. Schlabach, M. Bruns, D. V. Szabó, J. Haußelt, *Plasma Process. Polym.* **2007**, *4*, 865.
- [3] L. A. O'Dell, S. L. P. Savin, A. V. Chadwick, M. E. Smith, *Nanotechnology* **2005**, *16*, 1836.
- [4] Y. Al-Angrý, S. L. P. Savin, K. E. Rammutla, M. J. Pooley, E. R. H. Van Eck, A. V. Chadwick, *Radiat. Eff. Defects Solids* **2003**, *158*, 209.
- [5] N. L. Wu, S. Y. Wang, I. A. Rusakova, *Science* **1999**, *285*, 1375.
- [6] D. V. Szabó, S. Schlabach, R. Ochs, B. Schumacher, M. Bruns, *Ceram Forum Int.* **2007**, *84*, 7.
- [7] H. H. Brongersma, M. Draxler, M. de Ridder, P. Bauer, *Surf. Sci. Rep.* **2007**, *62*, 63.
- [8] V. Trouillet, H. Troesse, M. Bruns, E. Nold, R. G. White, *J. Vac. Sci. Technol., A* **2007**, *25*, 927.
- [9] K. L. Parry, A. G. Shard, R. D. Short, R. G. White, J. D. Whittle, A. Wright, *Surf. Interface Anal.* **2006**, *38*, 1497.
- [10] J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129.
- [11] G. P. López, D. G. Castner, B. D. Ratner, *Surf. Interface Anal.* **1991**, *17*, 267.
- [12] I. Tunc, S. Suzer, M. A. Correa-Duarte, L. M. Liz-Marzan, *J. Phys. Chem. B* **2005**, *109*, 7597.
- [13] M. P. Seah, S. J. Spencer, *Surf. Interface Anal.* **2002**, *33*, 640.
- [14] M. P. Seah, R. White, *Surf. Interface Anal.* **2002**, *33*, 960.
- [15] J. C. Sánchez-López, A. Fernández, *Surf. Interface Anal.* **1998**, *26*, 1016.
- [16] S. Tanuma, C. J. Powell, D. R. Penn, *Surf. Interface Anal.* **1991**, *17*, 927.
- [17] Z. H. Lu, J. P. McCaffrey, B. Brar, *Appl. Phys. Lett.* **1997**, *71*, 2764.
- [18] P. J. Cumpson, M. P. Seah, *Surf. Interface Anal.* **1997**, *25*, 430.
- [19] S. Tanuma, in *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy* (Eds: D. Briggs, J. T. Grant), IM Publications and Surface Spectra Limited: Chichester, **2002**.

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