DOI 10.5162/IMCS2018/P2GS.6

In situ resistance monitoring during deposition of flame-made chemoresistive gas sensing films

Christoph O. Blattmann, Andreas T. Güntner and Sotiris E. Pratsinis
Particle Technology Laboratory, ETH Zurich, CH-8092 Zurich, Switzerland
sotiris.pratsinis@ptl.mavt.ethz.ch

Abstract

Flame-deposited semiconducting nanomaterials on microelectronic circuitry exhibit exceptional performance as chemoresistive gas sensors. Current manufacturing technology, however, does not monitor *in situ* the formation of such nanostructured films even though this can facilitate the controlled and economic synthesis of these sensors. Here, the resistance of such growing films is measured *in situ* during fabrication to monitor the creation of a semiconducting nanoparticle network for gas sensors. Upon formation of that network, the film resistance drops drastically to an asymptotic value that depends largely on film structure and morphology rather than on its thickness and nanoparticle size. Sb-doped SnO_2 sensing films of different morphologies exhibit different characteristic *in situ* resistance patterns. The above understanding enables the rapid and economic flame-synthesis of thin gas sensors consisting of minimal nanomaterial mass, possessing a tuned baseline resistance and exhibiting excellent response to ethanol vapor.

Key words: tin oxide, flame-spray pyrolysis, thin film, surface growth, fabrication control

Introduction

Gas sensors made by direct flame-deposition are attractive for their highly porous and crack-free[1] sensing films. They are composed of high surface area nanoparticles with diverse composition tuned for ppb-level sensitivity and high selectivity towards key analytes such as Si-doped WO_3 and MoO_3 for acetone[2] and ammonia,[3] respectively, or Ti-doped ZnO for isoprene.[4] Such sensors are attractive for healthcare monitoring by non-invasive breath analysis.[5] Fabrication development has also led to the ability to process flame-made sensors by techniques compatible with standard silicon-wafer micromachining. This enables the preparation of low power sensors and highly sensitive sensor arrays[6] that are attractive for portable hand-held devices.[7]

So far the development of such sensors has been focused mostly on material composition and to a lesser extent on film morphology. However, optimizing the latter could boost analyte response as well as reduce the corresponding response/recovery times. Measuring the *in situ* resistance during flame-deposition of nanostructured films offers fabrication control by providing immediate feedback when an interconnected film is created.[7] Thus by monitoring the resistance of semiconducting films during their deposition, it is possible to prepare gas sensing films of minimal thickness and optimal resistance in a reproducible and economical manner.[8]

This work focuses on *in situ* monitoring the resistance of nanostructured films fabricated by direct deposition of flame-made Sb-doped SnO_2 nanoparticles.[8] The sensing film morphology was tuned by a substrate-impinging particle flame fed by a precursor solution containing varying metal ion concentrations. *In situ* resistance monitoring enabled control over final film resistance as well as direct insight into network formation and nanoparticle growth, necking and coalescence. The performance of these films as ethanol vapor sensors was assessed and related to their *in situ* resistance and nanoparticle film characteristics.

Experimental

Gas sensing nanoparticle films were prepared by direct deposition of flame-made Sb-doped (12 at%) SnO_2 onto alumina substrates with interdigitated platinum electrodes. Deposition was carried-out for up to 6 min. Substrate preheating, film deposition and cooling to room temperature was closely monitored by the *in situ* resistance (R_i) between the interdigitated electrodes with a multimeter (Tektronix DMM4050).

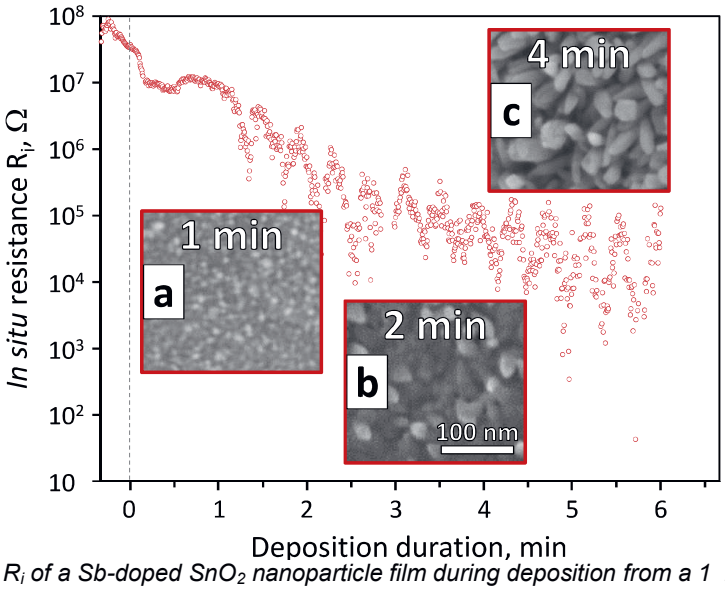

Fig.1 In situ resistance R_i of a Sb-doped SnO_2 nanoparticle film during deposition from a 1 mM precursor solution. Prior to deposition, the substrate is preheated for 20 s (dashed line). Insets (a-c) show top view SEM images of these Sb-doped SnO_2 nanoparticle films deposited for 1 (a), 2 (b) and 4 minutes (c). All images are at the same magnification. Adapted from [8].

Results and Discussion

Figure 1 shows the *in situ* film resistance as a function of Sb-doped SnO_2 deposition duration using a 1 mM FSP precursor solution concentrations (PSC). At the start of deposition (t =0 min) R_i exhibits a PSC-dependent reduction. At low PSC as shown in Fig. 1, the R_i remains at first (up to ca. 1 min) rather indifferent to nanoparticle deposition as it takes some time to build the interconnected particle bridges. But as deposition is prolonged (t >1.5 min), the R_i starts to drop. This clearly indicates the formation of an interconnected network of nanoparticles as is inferred from SEM images of such films deposited for 1 (Fig. 1a), 2 (b) and 4 min (c). Also quite notable is the strong oscillation of R_i by more than an order of magnitude (Fig. 1) during network formation. This stems from the constant formation (by deposition) and break-up of necked nanoparticles (by coalescence) on the substrate (e.g. repeatedly from lace-like to cauliflower-like structures) during flame-deposition.

As a result, the film formation and morphology of Sb-doped SnO_2 is monitored during direct flame-deposition.[8] This monitored R_i is correlated to its evolving particle size and necking enabling the ability to optimize material quantity, fabrication time and also the final film resistance. This leads to the ability to rapidly synthesize thin flame-made gas sensors with improved analyte response and reduced response/recovery times.

References

[1] L. Mädler et al., Direct formation of highly porous gas-sensing films by in situ thermophoretic deposition of flame-made Pt/SnO_2 nanoparticles, *Sens Actuators B*, 114(2006) 283-95. doi: 10.1016/j.snb.2005.05.014

[2] M. Righettoni, A. Tricoli, S.E. Pratsinis, Si:WO_3 Sensors for Highly Selective Detection of Acetone for Easy Diagnosis of Diabetes by Breath Analysis, *Anal Chem*, 82(2010) 3581-7. doi: 10.1021/ac902695n

[3] A.T. Güntner, M. Righettoni, S.E. Pratsinis, Selective sensing of NH_3 by Si-doped α-MoO_3 for breath analysis, *Sens Actuators B*, 223(2016) 266-73. doi: 10.1016/j.snb.2015.09.094

[4] A.T. Güntner, N.J. Pineau, D. Chie, F. Krumeich, S.E. Pratsinis, Selective sensing of isoprene by Ti-doped ZnO for breath diagnostics, *J Mater Chem B*, 4(2016) 5358-66. doi: 10.1039/C6TB01335J

[5] A.T. Güntner et al., Noninvasive Body Fat Burn Monitoring from Exhaled Acetone with Si-doped WO_3-sensing Nanoparticles, *Anal Chem*, 89(2017) 10578-84. doi: 10.1021/acs.analchem.7b02843

[6] A.T. Güntner et al., E-Nose sensing of low-ppb formaldehyde in gas mixtures at high relative humidity for breath screening of lung cancer?, *ACS Sens*, 1(2016) 528-35. doi: 10.1021/acssensors.6b00008

[7] C.O. Blattmann, S.E. Pratsinis, In situ measurement of conductivity during nanocomposite film deposition, *Appl Surf Sci*, 371(2016) 329-36. doi: 10.1016/j.apsusc.2016.02.240

[8] C.O. Blattmann, A.T. Güntner, S.E. Pratsinis, In Situ Monitoring of the Deposition of Flame-Made Chemoresistive Gas-Sensing Films, *ACS Appl Mater Interfaces*, 9(2017) 23926-33. doi: 10.1021/acsami.7b04530