Size-selected agglomerates of SnO₂ nanoparticles as gas sensors

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The effect of nanoparticle structure on gas sensing performance is investigated. Size-selected nanostructured SnO₂ agglomerate particles for gas sensors were made by scalable flame spray pyrolysis. These particles were polydisperse (up to 12 μm in diameter) and consisted of primary particles of 10 nm in grain and crystal size as measured by transmission electron microscopy, x-ray diffraction, and Berner low pressure impactor (BLPI). The effect of agglomerate size on thermal stability and sensing of ethanol vapor (4–100 ppm) and CO (4–50 ppm) was investigated by selecting nearly monodisperse fractions of these agglomerates by the BLPI. Sensor layers made with these size-fractionated agglomerates exhibited higher thermal stability and dramatically enhanced sensitivity for both analytes than layers made with polydisperse agglomerates. This is attributed to their aggregate (or hard agglomerate) structure exhibiting small sinter necks between their constituent primary particles of tin dioxide that had also a narrow size distribution as expected for particles generated in flames. Upon further sintering of these optimally sized, nanostructured agglomerates, grain and neck growth degraded their superior sensitivity, supporting the proposed mechanism of their enhanced sensitivity: optimal primary particle necking. © 2009 American Institute of Physics. [doi:10.1063/1.3212995]

I. INTRODUCTION

Non-invasive and early detection of illnesses such as diabetes or asthma by acetone vapor¹ or CO (Ref. 2) concentrations, respectively, in patients' breath has motivated the development of highly sensitive and selective gas sensors. In fact, asthmatic patients have only 1–2 ppm higher CO concentration in their breath than healthy people.² Very recently, emphasis has been placed in developing sensors for non-invasive medical diagnostics such as electrospin polyaniline hybrids for detection of NO₂ and pH in the human breath that are associated with pulmonary diseases.³ Similarly, highly sensitive and selective Cr-doped WO₃ sensors were able to detect acetone down to 0.2 ppm.⁴

Metal oxides such as SnO₂ are widely applied for gas detection as their sensitivity and low limit of detection can be enhanced by decreasing particle size below 10 nm.⁵ Kennedy *et al.*⁶ selected nearly monodisperse nanosized SnO₂ particles by a differential mobility classifier from polydisperse ones made by evaporation-condensation in a hot-wall reactor. By decreasing the particle size from 35 to 10 nm, the sensitivity to 1000 ppm ethanol was nearly tripled.⁶ However, the sensitivity improvement by reducing the sensor particle size is usually short lived as the thermal stability of these particles is very low.⁷ So, even highly sensitive nanoparticles will grow to larger ones, unless their sintering is inhibited.⁸ This can be achieved by doping SnO₂ with other oxides like SiO₂.⁹ Doping, however, may not be always desirable as it adds another component to the sensor

and its uniform distribution may not be always assured.¹⁰ The thermal stability of nanoparticles, however, is affected also by their size distribution.¹¹ Polydisperse particles have lower thermal stability than monodisperse of equal average size as the former sinter faster than the latter leading to grain growth and uneven sinter necks.¹¹ Thus, by narrowing the size distribution, the thermal stability of nanoparticles could be enhanced also.

Here, the effect of agglomerate size distribution on sensor performance is investigated for SnO₂ particles made by scalable flame spray pyrolysis (FSP).¹² The FSP has distinct advantages over traditional wet-chemistry processes that are used for synthesis of gas sensors.¹³ The FSP is a fast process resulting in highly pure products of unique phase composition without liquid byproducts.¹⁴ Nanostructured single¹⁵ and mixed oxides¹⁰ have been made by FSP up to 1 kg/h. Such particles, however, are polydisperse consisting of primary particles, and hard (chemically or sinter-bonded primary particles) and soft agglomerates (physically bonded particles)¹⁵ with well controlled morphology and primary particle and crystal size.¹⁴ Furthermore, FSP-made SnO₂ particles have been used to detect NO_x, propanal, CO, and ethanol.^{9,13,16,17} Also such particles can be deposited directly and adhere well on state-of-the-art microsensors.¹⁸ Doping with SiO₂ inhibits SnO₂ sintering and thus nanostructures with optimal sinter neck size (twice their Debye length) can be made having substantially enhanced (about ten times higher) thermal stability and sensitivity than conventional sensors.⁹

Here, FSP is used to make SnO₂ particles from which nearly monodisperse agglomerate fractions are selected by a cascade Berner low pressure impactor (BLPI).¹⁹ The thermal

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FIG. 1. (Color online) The FSP reactor (a) and particle collection unit by impactor (b) and filter (c).

stability of these agglomerates is investigated and compared to polydisperse ones. Sensors made with such agglomerates are evaluated for sensing ethanol vapor and CO along with their long term stability and reproducibility. Finally, it is shown that by controlling the polydispersity of these agglomerates, the sensing performance can be greatly enhanced. The existence of such superior sensitivity is explored further by progressive sintering of these monodisperse agglomerates and monitoring their sensing performance.

II. EXPERIMENTAL

A. Nanoparticle synthesis, collection, and size distribution measurements

A precursor solution containing 0.5M tin(II)-ethylhexanoate (Sigma Aldrich, purity >98%) in xylene (Fluka, purity >98%) was fed at a rate of 5 ml/min through the FSP-nozzle and dispersed with 5 l/min oxygen (Pan Gas, 99.5%) with a pressure drop of 1.5 bars at the nozzle outlet.¹³ This spray was ignited by an annular premixed methane/oxygen flame ($\text{CH}_4=1.5$ l/min and $\text{O}_2=3.2$ l/min) surrounding the nozzle. Additionally, 5 l/min of oxygen

were supplied by a surrounding porous ring to assure overstoichiometric combustion conditions [Fig. 1(a)].

The SnO_2 particles were collected 70 cm above the flame either by a cascade impactor or a glass-fiber filter (GF/D Whatman, diameter of 257 mm) in a water-cooled holder [Figs. 1(b) and 1(c)]. The cascade impactor had ten stages and one prestage to cutoff particles larger than 16 μm in aerodynamic diameter. Each stage consists of a set of jet orifices drilled concentrically, except for stage 1 that has two such concentric circles of orifices.¹⁹ The stages are numbered so that the first stage has the smallest cutoff diameter (Table I). The main characteristics of the BLPI are summarized in Table I. The pressure after last stage was 10.1 kPa. The Peclet numbers²⁰ estimated from the aerodynamic agglomerate diameters and jet velocities (Table I) increased from 0.038×10^4 to 1659×10^4 for stages 1–10. The impactor inlet with a sampling line of 80 cm was placed 70 cm above the FSP-nozzle collecting nearly monodisperse agglomerates [Fig. 1(b)] on its ten stages, with an aerodynamic cut point particle diameter²⁰ range $d_a=0.04$ –11.5 μm (Table I). Greased (Api-azon) aluminum-foil collection substrates were used in the impactor to avoid particle rebound. For the gravimetric mass size distribution analysis, the foils were weighted before and after collection. The collection time was 3–4 min. The impactor (wall) temperature was below 40 °C during collection. The agglomerate aerodynamic mode (d_{ao}) and geometric mean (d_{ac}) diameters²⁰ were obtained from the impactor mass size distribution.

B. Particle and layer characterization

Particles were collected also thermophoretically within 40 ms (Ref. 21) on (TEM) transmission electron microscopy grids (carbon type B copper 200 mesh, Ted Pella, Inc.) 13 cm above the FSP-nozzle to assure complete droplet evaporation.^{12,22} The x-ray diffraction (XRD) patterns were measured by Bruker AXS D8 Advance (40 kV, 40 mA) and crystal characteristics were obtained using TOPAS 3.0 software (Bruker). So crystal sizes (d_{XRD}) were obtained by the Rietveld method²³ with the structural parameters of SnO_2 (ICSD Coll. Code 084576; Bolzan *et al.*, 1997). Additionally, the bimodality of crystal size was obtained by fitting two superimposed modes of SnO_2 to the entire XRD spectrum without changing lattice constant.²⁴ Selected area electron diffraction and TEM were carried out with a Phillips CM30ST microscope (LaB6 cathode, 300 kV). The image analysis for primary particle size distribution was carried out with OPTIMAS software (Media Cybernetics) measuring 436 particles and obtaining the count mode (d_{po}) and geometric mean (d_{pe}) diameters.²⁰ The average porosity of impactor

TABLE I. Characteristics for each BLPI stages. For sensor fabrication, deposits from stages 2–4 were used.

Impactor stage	1	2	3	4	5	6	7	8	9	10
d_a (nm)	42	68	118	236	414	724	1409	2810	5650	11530
Jet velocity, u (m/s)	277	256	209	243	112	61	24	10	5	3
Number of Nozzles	232	116	116	25	22	25	46	44	24	12
Diameter of nozzle (mm)	0.3	0.3	0.3	0.4	0.5	0.6	0.7	1.1	2.1	4.2
Peclet number ($\times 10^4$)	0.038	0.26	1.9	23	55	106	179	314	654	1659

deposits that exhibited typically a conical shape²⁰ as obtained by optical microscopy (Zeiss, Axio Cam MRc camera and Zeiss, Axio plan microscope, Germany) was estimated by

$$\varphi = 1 - \frac{m_i}{\rho V_c N_c}, \quad (1)$$

where ρ is the SnO₂ bulk density (6.89 g/cm³), V_c is the volume of the average conical deposit, m_i is the total mass on the i th impactor stage, and N_c is the number of conical deposits in stage i corresponding to the number of nozzles in stage i (Table I). The scanning electron microscopy analysis of impacted cones and sensing layers was performed on a LEO 1530 Gemini (Zeiss/LEO, Oberkochen) microscope. The crystal growth of filter- and BLPI-collected particles (Table I) was measured by heating (20 °C/min) them to 400–900 °C in an oven (Carbolite, CWF 1300, Germany) and keeping them there for 12 h.

C. Sensor fabrication and characterization

First, a viscous paste was prepared by adding to α -terpineol 2.4 wt % ethylcellulose and 17 wt % of FSP-made SnO₂ particles collected on filter²⁵ and impactor stages (Fig. 1). This paste was stirred for 30 min and doctor bladed on Al₂O₃ substrates with interdigitated Au electrodes (10 × 10 mm², Electronics Design Center, Micro Fabrication Lab, Case Western Reserve University). The films were 15 μ m thick. They were heated at 0.5 °C/min stepwise to 50 and 100 °C and kept at constant temperature for 1 h, then at 2 °C/min to 400 °C and kept for 2 h, then 20 °C/min to 600 °C and kept 12 h, and finally cooled down to room temperature at 5 °C/min.²⁵ The sensors were made with commercial SnO₂ powder (Sigma-Aldrich, d_{XRD} = 50 nm) or FSP-made ones collected either on filter [Fig. 1(c)] or on single (2, 3, or 4) or combined impactor stages 2–4 [Fig. 1(b), Table I].

The change in sensor resistance upon exposure to CO (4–50 ppm) and ethanol vapor (4–100 ppm) in dry air (79% N₂, 21% O₂, PanGas) at 420 or 320 °C (Ref. 8 and 26) respectively, was measured in dc mode.²⁵ The sensor was placed in the center of a quartz tube (3.5 cm diameter and 90 cm length) which in turn was introduced into a tubular furnace (Nabertherm). The tube was filled with silicon carbide (1 mm grains) upstream of the sensor to homogenize the analyte gas flow. Gold wires were connected with a Ag paste to the sensor electrodes and externally connected to a digital multimeter (Keithley 2700 multimeter) recording the sensor resistance. A Ni–CrNi thermocouple (MDW GmbH, DIN IEC 584 Type K) was used to monitor sensor temperature. The furnace was heated at 15 °C/min to reach 420 °C for CO and 320 °C for ethanol vapor and kept there during both tests. A total gas flow rate was 1 l/min. Typically the sensor was exposed to dry synthetic air and the baseline (at 420 or 320 °C) was achieved in 4 ± 0.5 h for each sensor test (Table II). After stepwise exposure to CO or ethanol vapor, the sensor was again exposed to pure synthetic air until the baseline was recovered. The baseline resistance varied from 2 to 20 M Ω at 420 °C and from 10 to 100 M Ω at 320 °C with all sensors. The sensor response (S) is the ratio

TABLE II. Reproducibility (Q_r) and stability (Q_s) of sensors made from different impactor- and filter- collected powder (S to 10 ppm CO in dry air at 420 °C).

Sensor made from	Reproducibility (%)	Stability (%)
Stage 2	93	93
Stage 3	73	84
Stage 4	78	85
Stages 2–4	95	...
Filter	96	95

$R_{\text{air}}/R_{\text{gas}}$, where R_{air} and R_{gas} are the sensor resistances in pure and analyte-containing dry air, respectively.

Four day stability tests were performed while reproducibility was obtained with duplicates. To compare stability (Q_s) and reproducibility (Q_r), the mean value and standard deviation of sensor response (S) from n (4 days or 2 sensors) tests is evaluated:¹⁷

$$Q_j = \frac{\frac{1}{n} \sum_{k=1}^n S_k}{S_{\text{max}}} \times 100, \quad (2)$$

where $j=r$ or s , so at $Q_j=0\%$ the sensor is completely irreproducible or unstable and if $Q_j=100\%$ the sensor is perfectly reproducible or stable.

III. RESULTS AND DISCUSSION

A. Agglomerate size and morphology

The as-prepared FSP-made SnO₂ particles consist of agglomerated crystalline primary particles¹³ with a d_{XRD} of about 10 nm [Figs. 2(a)–2(d)]. The count mode (d_{po}) and geometric mean (d_{pe}) diameters of the primary particles were 9.5 and 10.4 nm [Fig. 2(e)] in agreement with their d_{XRD} indicating that they were monocrystalline while their geometric standard deviation [GSD (Ref. 20)] was 1.4. The primary particle range was 2–60 nm in diameter [Fig. 2(e)]. The GSD is slightly narrower than that of the self-preserving size distribution of coagulating aerosols, most probably by sintering of primary particles into hard agglomerates (aggregates)²⁷ as indicated by their sinter necks [Fig. 2(b)]. The aggregate structure with sinter neck sizes comparable to twice the Debye length of SnO₂ may exhibit high sensitivity by completely depleted intercrystal boundaries (“bottle-neck” morphology²⁸).

Figure 3(a) shows polydisperse particles collected by thermophoretic sampling. Their mass was distributed over ten impactor stages [Fig. 3(b)] with $d_a=0.04$ –11.5 μ m (Table I). More than 93% by mass of the produced agglomerates was under 1 μ m. The aerodynamic (d_a) mode and geometric mean diameters of the agglomerate mass size distribution were $d_{a0}=118$ and $d_{ae}=162$ nm, respectively, with a GSD of 3.6 [Fig. 3(a)].

Figure 4 shows particle deposits from impactor stage 3. They are conically shaped [Fig. 4(a)] with a relatively dense, layered morphology (Figs. 4(b) and 4(c)). Their porosity [Eq.(1)] is $\sim 80 \pm 5\%$ (stages 2–4, with increasing Pe from

FIG. 2. Images [(a) and (b)], ED (c), and XRD patterns of FSP-made SnO_2 powder collected on the filter. Aggregates and agglomerates of primary particles (a) with sinter necks (b) are highly crystalline [(c) and (d)] with a lognormally shaped count size distribution (e).

2600 to 230 000, Table I) which is smaller than that of thermophoretically deposited films (porosity $\sim 98\%$, at $Pe < 0.01$) (Ref. 17) but similar to that for films deposited by impaction.²⁹ Present porosities are slightly lower than the latter as polydisperse particles are employed here.

Figure 5 shows the XRD spectra [(a) and (b)], images [(c) and (d)], and electron diffraction (ED) patterns [(e) and (f)] from the first ($d_a = 42$ nm) and eight ($d_a = 2.8$ μm) impactor stages [Fig. 3(b)]. In contrast to increasing primary particle size with increasing aerodynamic diameter for atmospheric aerosols,³⁰ here, the geometric mean diameter of the primary particles (d_{TEM}) was constant (11 ± 0.5 nm) in

FIG. 3. Image of agglomerated SnO_2 particles collected by thermophoretic sampling above the flame tip (a) and agglomerate mass size distribution from stages 1–10 measured by gravimetric analysis of BLPI deposits (b). The particles were highly agglomerated (a) and the mode diameter (d_{a0}) was at 118 nm (average of 20 impactor samples).

FIG. 4. Various magnifications of conical agglomerate SnO_2 deposits as deposited on impactor stage 3 [(a)–(c)]. The porosity of these cones was $\sim 80\%$.

FIG. 5. XRD spectra [(a) and (b)], images [(c) and (d)], and ED-patterns [(e) and (f)] from agglomerated particles collected on stage 1 with $d_a = 42$ nm [(a), (c), and (e)] and stage 8 with $d_a = 2.8$ μm [(b), (d), and (f)]. The spectra of stage 1 (a) revealed a unimodal crystal size of 10 nm while stage 8 (b) had a bimodal crystal size distribution with 80% of the mass at 7 nm and 20% at 25 nm.

FIG. 6. Crystal size of the polydisperse filter collected (diamonds) and combined impactor stages 2–4 (stars) as well as nearly monodisperse agglomerates from single impactor stages 2, 3, and 4 (circles, triangles, and squares) as a function of sintering temperature after 12 h.

stages 2 (109 particles counted), 3 (90 particles counted), and 4 (128 particles counted). Atmospheric aerosols are made from different sources so they contain a broader distribution of primary particles than engineered aerosols here. Aggregates of the latter are made of narrowly distributed primary particles by coagulation and sintering.²⁷ Furthermore, the average crystal size was constant ($d_{\text{XRD}} = 10$ nm) and no difference in primary particle morphology was observed here for all impactor stages or agglomerate sizes [Figs. 3(b) and 5(a)–5(d)]. However, detailed analysis of the XRD spectra revealed a bimodal crystal size distribution for stages 7 and 8. Modes with average crystal size of ~ 25 nm (20% of the total mass) and 7 nm (80% of the mass) were observed for stages 7 and 8 [Fig. 3(a), Table I]. This is in agreement with the ED patterns of stage 8 [Fig. 5(f)] indicating the presence of large (bright spots) and small (bright rings) crystals. As at these stages the largest agglomerates are collected, it is quite likely to contain broad or even a bimodal distribution of large and fine crystals that experienced different residence times at high temperatures. Such bimodal crystals may have been formed in the inner and outer flame regions.³¹

B. Thermal stability

Under thermal stress, sintering takes place between primary particles in agglomerates. Figure 6 shows the sintering of particles collected on filter (diamonds), single impactor stages 2 (circles), 3 (triangles), and 4 (squares), or combined ones (stars) (Table I). The crystal size of more monodisperse particles from single stages 2–4 increases from 10 to 32–36 nm with increasing temperature from 25 to 900 °C. Stage 2 particles exhibit the smallest crystal size after such annealing. The crystal growth of polydisperse filter-collected (Fig. 6, diamonds) or impactor-collected powders from the combined stages (Fig. 6, stars) at 700–900 °C is slightly larger than from single impactor stages. The small crystal size differences between the monodisperse agglomerate sizes at 700–900 °C is attributed to the broader polydispersity at larger stages than at smaller ones as indicated by XRD and ED patterns since fine particles were attached to larger ones. In fact, sintering of polydisperse particles is faster than for monodisperse ones¹¹ as with polydisperse ag-

FIG. 7. High resolution TEM images from filter-collected polydisperse (a) and nearly monodisperse impactor-collected particles from impactor stage 2 (b) after sintering at 600 °C for 12 h. The necking by sintering is more developed between initially polydisperse agglomerates [(a), 1] than between nearly monodisperse ones [(b) 2 and 3, respectively].

glomerates here. Sintering is slower and can lead to smaller crystals for nearly monodisperse agglomerates (e.g., 32 nm for stage 2 agglomerates annealed 900 °C) than for polydisperse ones (e.g., 39 nm for filter-collected agglomerates annealed at 900 °C). Images after sintering at 600 °C indicate that smaller sintering necks are formed for the nearly monodisperse agglomerates of stage 2 [Fig. 7(b)] than the filter-collected polydisperse ones [Fig. 7(a)].

C. Sensor performance and stability

All sensors were annealed at 600 °C for 12 h before testing to stabilize them and avoid sintering during such measurements ($T = 320$ – 420 °C). The sensors' response to ethanol vapor is shown in Fig. 8. Sensors made from commercial powder (Fig. 8, hexagons, $d_{\text{XRD}} = 50$ nm) have lower response than any FSP-made ones that are finer in crystal size ($d_{\text{XRD}} \sim 15$ nm after 600 °C, Fig. 6). The sensors made with the nearly monodisperse agglomerates from stages 2–4 (Fig. 8, squares, triangles, and circles) have higher response than polydisperse ones (Fig. 8, diamonds). In fact, the response increased with decreasing agglomerate size or stage No. (Fig. 8) indicating that finer agglomerates might be better sensors.

The responses to 100 ppm ethanol vapor are extremely high, e.g., $S = 640$ for the sensor made with agglomerates from stage 2. For comparison, six times smaller response was obtained to the same ethanol concentration from sol-gel made sensors.³² Sensors made by combustion chemical vapor deposition exhibited $S = 280$ – 100 ppm ethanol³³ which is 60% lower than the highest detected here (Fig. 8, circles). Such high sensitivities as here (e.g., $S = 380$ at 50 ppm etha-

FIG. 8. Sensor response to ethanol vapor of SnO_2 sensors made from commercial powder (hexagons), filter-collected (diamonds), and impactor-collected FSP-made powder from stages 2 (circles), 3 (triangles) and 4 (squares) in dry air at $T=320^\circ\text{C}$.

nol vapor) have been achieved only by optimal SiO_2 doping of FSP made and directly deposited SnO_2 films ($S=320$ at 50 ppm ethanol vapor).⁹

Figure 9 shows the response to CO of a sensor made with the filter-collected SnO_2 particles. The CO reduced the sensor resistance from 20 to 5 M Ω at 4 ppm and to 4.2 M Ω at 5 ppm CO as expected for n-type semiconductors.⁸ That way, the sensor was able to decipher down to 1 ppm differences in CO concentration. Detection of such small differences may help to distinguish between healthy and asthmatic patients from breath analysis.²

Figure 10 shows the response to CO by sensors with commercial and FSP-made powder collected from the filter and from single and combined impactor stages. The sensor made from commercial powder has lower response to CO than FSP-made sensors similar to ethanol due to its substantially larger crystal size. Likewise, sensors made from polydisperse powder (combined impactor stages or filter) have lower response to CO than sensors made from single impactor stages. As discussed above for ethanol, this stems with the poorer thermal stability (Fig. 6) and larger sinter necks of polydisperse than monodisperse powders (Fig. 7). In fact, the

FIG. 9. Sensor resistance from filter-collected powder in dry air (baseline) and under exposure to various CO concentrations at 420°C .

FIG. 10. Sensor response to CO of SnO_2 sensors made from commercial powder (hexagons), filter-collected (diamonds), and impactor-collected FSP-made powder from combined stages (stars) as well from single stages 2 (circles), 3 (triangles), and 4 (squares) in dry air at $T=420^\circ\text{C}$.

latter exhibited twice as high response to CO than polydisperse ones. The best response, $S=32$ at 50 ppm CO, was obtained from the sensor made with the smallest (stage 2) agglomerates. This is nine times higher than for FSP-made and directly deposited SnO_2 films.¹⁷ Such high response to CO, e.g., $S=12$ at 10 ppm and 420°C as here have not been reached earlier for FSP-made pure or even Pt-doped SnO_2 -sensors.^{12,16,17} In fact, at 10 ppm CO, sensitivities of ~ 4 were obtained for optimally Pt-doped SnO_2 at 400°C (Ref. 16) while sensitivities of about 2 were obtained for sol-gel made SnO_2 films.³⁴

To better understand the superior sensing performance for CO and ethanol vapor by sensors made with monodisperse agglomerated SnO_2 particles, one needs to take a closer look to the structure of these particles. Figures 11(a) and 11(b) shows a schematic of two SnO_2 grains in air at 320 or 420°C . Oxygen ions are adsorbed on the grain surface scattering electrons within the Debye length (δ) in this depleted area so the SnO_2 conductivity is drastically reduced.²⁸ The

FIG. 11. Schematic of the two SnO_2 grains in air at 320 or 420°C . Oxygen ions are adsorbed on the grain surface [(a) and (c)]. These oxygen ions scatter electrons within the Debye length $\delta=3.2\text{--}3.5\text{ nm}$ forming an electron depleted region close to the surface (Ref. 28). Desorption of oxygen ions due to reaction with ethanol vapor or CO reduces the depleted regions [(c) and (f)]. For large sintering necks, the conductivity is controlled by the width of the conduction channel [(a) and (b)] leading to small sensor responses. In contrast, for bottle-neck morphology (c) neck size smaller than two times Debye length ($2\delta=6.4\text{--}7\text{ nm}$), the conduction channel will form only after desorption of the oxygen ions (d) leading to significant change in grain resistance and high sensor response (Refs. 9 and 28).

FIG. 12. Sensor response (in dry air at $T=320^\circ\text{C}$) to 50 ppm ethanol vapor of the polydisperse filter-collected (diamonds) and nearly monodisperse agglomerates from impactor stage 2 (circles) as function of sintering temperature.

Debye length (δ) depends on the SnO_2 properties and temperature, so it is 3.2 nm at 320°C and 3.5 nm at 420°C .²⁸ Due to the small size of δ , the grain and neck sizes have an important role: if the neck size is larger than 2δ [6.4 nm at 320°C and 7 nm at 420°C (Ref. 28)], a conduction channel with constant conductivity is formed in the core of the primary particles comprising the agglomerates.²⁸ Then, desorption of oxygen ions for reaction with ethanol vapor ($\text{C}_2\text{H}_5\text{OH} + \text{O}^- \leftrightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + e^-$) or CO ($\text{CO} + \text{O}^- \leftrightarrow \text{CO}_2 + e^-$) releases electrons widening the conduction channel [Fig. 11(c)] that results in moderate change in total conductivity and thereby small sensor response. In contrast, if the neck size is less than 2δ (bottle-neck morphology²⁸), the depleted region near the particle or grain surface dominates the particle conductivity by “opening” the conduction channel during desorption of oxygen ions [Fig. 11(d)].

As was shown in Fig. 7, neck growth is more advanced between initially polydisperse agglomerates [Fig. 7(a), number 1, neck size is 24 nm] than between nearly monodisperse ones [Fig. 7(b), numbers 2 and 3, neck sizes are 14 and 6 nm, respectively]. Therefore, it is expected that the nearly monodisperse particles with small bottle-neck [Figs. 11(b) and 11(d) (Ref. 9)] morphology have higher sensor response for ethanol vapor and CO (Figs. 8 and 9) than polydisperse ones with initially larger necks [Fig. 11(a)]. After sintering at 650°C , however, grain and neck growth reduced the high sensor responses from the size-selected agglomerates (Fig. 12). The response to 50 ppm ethanol vapor (Fig. 12, circles) of the sensor made with the smallest agglomerates (stage 2) dropped drastically from 380 to 170 after sintering for 12 h at 650°C due to transition from bottle- to open-neck morphology (Fig. 11). In contrast, the response of sensor made from the filter-collected particles dropped from 130 to only 100 ($\sim 25\%$) at the same sintering conditions (Fig. 12, hexagons), as these particles had already open neck morphology. After sintering for 12 h at 700°C , the response of both sensors (Fig. 12) decreased further from 170 and 100 to 100 and 72, respectively, by neck (Fig. 11), and even more by crystal growth (Fig. 6) consistent with the observed drop in specific surface area.^{16,18}

Even if sintering at high temperatures ($650\text{--}700^\circ\text{C}$) decreased the sensor response, the long term stability [Eq. (2)] at the operating conditions ($300\text{--}400^\circ\text{C}$) was between 84 and 95% (Table II). Values close to 100% have been achieved earlier for screen printed sensors.¹⁶ Here, the reproducibility of these sensors varied between 73% and 96%, while earlier directly deposited FSP-made sensors had only 71% reproducibility.¹⁷ Those sensors made from powders collected on the filter and the finest impactor stage 2 ($d_a = 68\text{ nm}$) had the highest long term stability and reproducibility of 93%–96% (Table II).

IV. CONCLUSIONS

Polydisperse agglomerates ($0.04\text{--}12\text{ }\mu\text{m}$) consisting of SnO_2 primary particles about 10 nm in grain and crystal size were produced by FSP. From these agglomerates, narrow size fractions were collected by impaction. Pastes of these particles were deposited by doctor blading onto Au electrodes. After annealing, the sensing performance and thermal stability of these sensors were investigated. Narrowly distributed agglomerates of different sizes ($70\text{--}240\text{ nm}$) exhibited outstanding sensing performance to CO and ethanol vapor and were more thermally stable than polydisperse ones containing identically sized SnO_2 crystals. The smaller the agglomerate size, the better is the sensor response to both analytes as well the higher thermal stability and reproducibility of these sensors. This superior performance is attributed to uniform neck size (comparable to twice the Debye length of SnO_2 crystals) between the SnO_2 primary particles leading to sintering inhibition and bottle-neck agglomerate morphology. In fact, sintering these agglomerates above 600°C increased the neck size between primary particles that drastically reduced their sensor response to ethanol vapor. The response to CO and ethanol vapor of sensors made with narrowly distributed agglomerate particles was maintained at typical operating conditions ($300\text{--}400^\circ\text{C}$).

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