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Comparison of gas sensor performance of SnO_2 nano-structures on microhotplate platforms

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ABSTRACT

Metal oxide nano-structures on microhotplate platforms have attracted a great deal of interest in gas sensor research for their potential to create both highly responsive and extremely portable gas sensors. Much of the current research on these sensors has focused upon the creation of hierarchical nanostructures, as van der Waals attraction between nanoparticles leads to agglomeration that impair sensor performance. In this research article, ink-jet printing onto microhotplates was explored as a method of avoiding nanoparticle agglomeration to produce an open film microstructure. Scanning electron microscopy was used to study the deposited thin nanoparticle film featuring an open microstructure free of large agglomeration. Sensor response and response times of ink-jet printed SnO_2 nanoparticles were found to be comparable to hierarchical particle films when exposed to methane and carbon monoxide in a background of dry air. Both the SnO_2 nanoparticles and microspheres had superior response compared to SnO_2 micron-size particles due to increased surface area of the nano-structures. This implies that proper control of the microstructure of the SnO_2 nanoparticle films produces similar gas sensor performance to SnO_2 hierarchical structures and has the potential for use in reproducibly manufacturing high-performance gas sensors.

1. Introduction

Recently, a drive towards miniaturized gas sensor platforms in the form of microhotplates, or MEMS (microelectromechanical system) devices has garnered increased attention for metal-oxide sensors [1–6]. The benefits of using microhotplate platforms include increased portability and reduced power consumption compared to traditional thick-film metal-oxide sensors on alumina substrates. Microhotplates are also advantageous for the growth of array technology to detect analyte gases in complex backgrounds.

In addition to the development of microhotplate platforms for miniaturized metal-oxide sensors, synthesizing oxide nano-structures with a specific morphology has led to increased gas sensor performance [7–11]. These nano-structures consist of a hierarchical structure with small clusters or sheets of particles connecting to form a micron-size particle with enhanced surface area compared to spherical particles. These nano-structures have been termed hierarchical nano-sheets [12], nano-structured microspheres [13], nano-flowers [14], and nano-urchins [15] as well as other descriptions in literature [16–18]. Hollow nano-structured microspheres are not being considered for this article.

These nano-structures benefit from having a large surface-to-volume ratio and a sensing layer consisting of a porous network of particles which allows quick access of the gas through the film [8,11]. Nanoparticles also display a high surface area and have been a focus of gas sensor research [19–21]. When nanoparticles are deposited and consolidate into a film, aggregation between the nanoparticles becomes very strong since van der Waals attraction is inversely proportional to particle size [22,23]. Nanoparticles prefer to combine and form large agglomerates which can serve as secondary particles [19]. Large agglomerates of nanoparticles have been shown to negatively influence sensor performance through decreased response and longer recovery times [7,8,10].

These nanoparticle films, which are heavily agglomerated, were printed using thick-film techniques on alumina sensor substrates. Thick-film printing is not applicable for microhotplate platforms due to the small size of the device and the likelihood of damaging the device during screen-printing. Our group has shown that nanoparticle films with an open microstructure free of agglomeration can be formed on microhotplate substrates using an ink-jet printer [24]. Ink-jet printing is an automated and reproducible deposition technique for producing thin films of oxide nanoparticles on microhotplate platforms [25]. The microstructure of the nanoparticle-film created by ink-jet printing maintains a large

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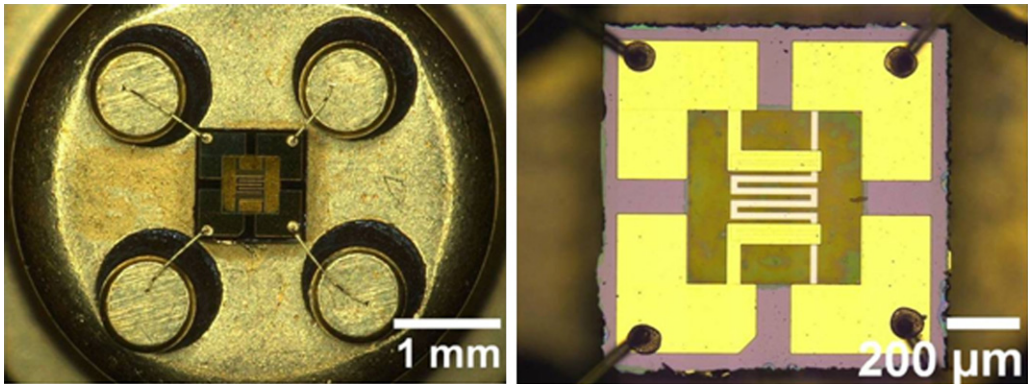

Fig. 1. Optical image of microhotplate device from Kebaili Corporation.

surface area similar to the nano-structured microsphere film. However, gas sensor experiments on miniaturized sensor substrates comparing non-agglomerated nanoparticles and nano-structured microspheres have not been thoroughly conducted.

The purpose of this research is to compare the gas sensor performance of SnO_2 nanoparticles with open microstructure (free of agglomeration), nano-structured microspheres, and micron-size particles on microhotplate platforms. The effect of particle size and the influence of the microstructure of the oxide-film on the response and transient effects of the sensor are presented. Gas sensor experiments to carbon monoxide (CO) for toxic detection and methane (CH_4) for explosion prevention were performed.

2. Materials and methods

2.1. SnO_2 nano-structures

SnO_2 nanoparticles were synthesized using a hydrothermal method modified from a synthesis technique used for Sb–SnO_2 nanoparticles [26]. Briefly, 12 mmol of micron-sized Sn powder (Sigma–Aldrich, USA) was mixed with 20 ml deionized water in a 45 ml Teflon® lined high temperature acid digestion vessel from the Parr Instrument Company. Ten ml of 70% HNO_3 was added to the mixture, and the container was sealed and heated at 225 °C for 15 h. The sample was allowed to cool, and the resulting material was centrifuged and washed to collect the precipitate.

SnO_2 nano-structured microspheres were synthesized using a hydrothermal method from literature for synthesizing particles that displayed response to ethanol gas [7]. Briefly, 1 mmol of $SnCl_2{\cdot}2H_2O$ and 4 mmol of oxalic acid ($H_2C_2O_4$) were added to 20 ml of deionized water in the Teflon-lined acid digestion vessel. To this mixture, 418 μl of 80% $N_2H_4{\cdot}H_2O$ solution was added, and the contents were sealed and placed in an oven at 180 °C for 14 h. The precipitates were washed, dried, and heat treated at 600 °C for 2 h. These particles are termed microspheres in this paper as a short-hand for nano-structured or hierarchical microspheres. Micron-size particles of SnO_2 from Sigma–Aldrich (−325 mesh powder) were used for evaluation of micron-size particle properties. No purification or treatment was conducted prior to use of the particles.

2.2. Deposition of particles on microhotplate substrates

Commercially available KMHP-100 microhotplates were purchased from the Kebaili Corporation (USA, Irvine, CA). Each microhotplate consists of a resistive platinum heater and pair of gold electrodes, allowing for both sample temperature control and resistance measurements. A calibration curve of temperature vs. voltage is supplied by the manufacturer for control of the oxide film temperature. Two optical images of a Kebaili microhotplate are shown in Fig. 1.

To enable deposition onto the microhotplate platforms, particle-laden ink suspensions were developed for compatibility with the ink-jet printer. Each ink was formed by mixing 15 ml of 50:50 wt% water:glycerol solution prior to the addition of SnO_2 particles. After the solution was thoroughly mixed, 1 wt% Bicine was added to the solution by sonication in a Branson Sonifier Model S-250D with a 1/2″ micro-tip. The solution was sonicated for 15 min, then 1 wt% SnO_2 powder was added and sonicated for 15 additional minutes. The powder consisted of SnO_2 nanoparticles, microspheres, or micron-size particles depending on the desired ink.

Nanoparticle inks were printed onto microhotplate substrates using a JetLab II ink-jet printing system purchased from MicroFab Technologies (USA, Plano, TX). To ensure uniform film thickness and complete coverage of the microhotplate electrodes, sample inks were deposited in a square 10 × 10 array of drops with 20 μm spacing between each drop. An optical image of SnO_2 nanoparticles deposited on a microhotplate via ink-jet printing is shown in Fig. 2. Due to their larger particle size, micron-size and microsphere particle-laden inks could not be printed using the JetLab II, and were instead deposited manually using a PV830 Pneumatic Picopump from World Precision Instruments [24]. After printing, samples were dried at 300 °C for 3 h and fired at 600 °C for 1 h.

2.3. Gas sensor testing

Gas sensor experiments were performed using a custom microhotplate testing facility. Samples were placed within a stainless

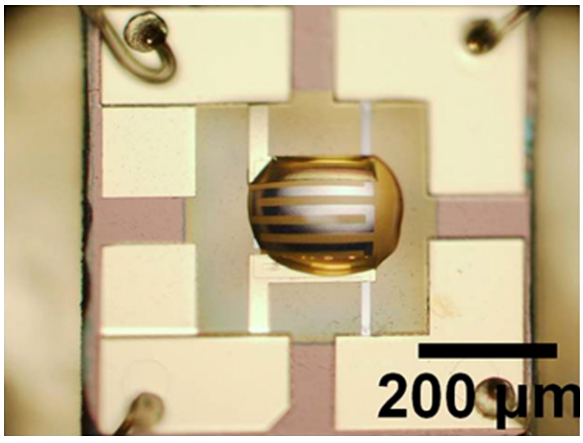

Fig. 2. Optical image of SnO_2 nanoparticle-laden ink deposited on a microhotplate via ink-jet printing.