Nanoparticle engineering and control of tin oxide microstructures for chemical microsensor applications

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Abstract

The use of metal nanoparticles as seed layers for controlling the microstructures of tin oxide (SnO₂) films on temperature controllable micromachined platforms has been investigated. The study is focused on SnO₂ due to its importance in the field of chemical microsensors. Nanoparticle seeds of iron, cobalt, nickel, copper and silver were formed by vapor deposition on the microhotplates followed by annealing at 500 °C prior to self-aligned SnO₂ deposition. Significant control of SnO₂ grain sizes, ranging between 20 and 121 nm, was achieved depending on the seed-layer type. A correlation was found between decreasing the SnO₂ grain size and increasing the melting temperature of the seed-layer metals, suggesting the use of high temperature metals as being appropriate choices as seed layers for obtaining a smaller SnO₂ grain structure. Smaller grain diameters resulted in high sensitivity in 90 ppm ethanol illustrating the benefits of nanoparticle seeding for chemical sensing. The initial morphology, particle size and distribution of the seed layers was found to dictate the final SnO₂ morphology and grain size. This paper not only demonstrates the possibility of depositing nanostructured oxide materials for chemical microsensor applications, but also demonstrates the feasibility of conducting combinatorial research into nanoparticle growth using temperature controllable microhotplate platforms. This paper also demonstrates the possibility of using multi-element arrays to form a range of different types of devices that could be used with suitable olfactory signal processing techniques in order to identify a variety of gases.

1. Introduction

The development of micro-electro-mechanical systems (MEMS)-based gas sensors is a rapidly growing area of research driven by the numerous advantages that can be realized with such microdevices, including low-power consumption, low cost due to batch fabrication, improved platform reliability, and improved selectivity through the use of arrays. Arrays of microfabricated sensors are attractive for making handheld electronic noses for applications such as environmental monitoring, pollution measurement, monitoring food freshness and medical diagnostics. Each of these applications requires sophisticated sensing systems, electronics for data acquisition, and signal processing for species identification and quantification.

Typically, semiconductor-metal-oxide gas sensors have polycrystalline thick or thin film oxide as the active sensing material. Tin oxide (SnO₂) is the most popular sensing film material due to advantages such as low cost, high sensitivity, and the ability to miniaturize and integrate on micromachined substrates [1–5]. Reducing gases are sensed due to change in the electrical resistance of the active SnO₂ sensing film at elevated temperatures. Catalytic metals such as platinum and palladium are often employed as surface dispersed additives on oxide gas sensors to improve sensitivity and selectivity [6–9]. However, the addition of catalytic metals results in loss of sensitivity over long periods of time due to fouling or coking of catalytic metals when exposed to certain gases and vapors [10].

Nanostructures of oxide materials are of considerable interest in the area of chemical sensing due to the improved sensitivity of nanostructures to reducing gases compared to the polycrystalline oxide materials [11, 12]. The improved sensitivity of the nanostructured oxides are due to the availability of high surface area grain boundary sites in nanostructured oxides compared to polycrystalline oxide materials [13, 14]. Furthermore, the higher gas sensitivities of nanostructures may make it possible to develop pure oxide sensing films that do not require catalytic additives for attaining acceptable performances. Chemically sensitive nanostructures integrated onto microsystems can pave the way for making portable chemical sensors for monitoring toxic gases in the field.

The first evidence that oxide nanoparticles improve sensitivity to reducing gases was obtained by Ogawa et al in 1982. Ogawa et al [15] measured the Hall parameters of ultrafine particles of SnO₂ in the size range between 5 and 20 nm in the presence of reducing gases. They reported an increase in carrier concentration and mobility as the concentration of reducing gas was increased. The conductivity, which is the product of carrier concentration and mobility, showed large gas concentration dependence. They concluded that ultrafine particles of SnO₂ are highly sensitive to gases and proposed an electrical conduction model based on particle size and Debye length or the depth of the space charge layer. The model predicts carrier mobility modulation with decreasing grain size. As the grain size becomes comparable to twice the Debye length, the mobility modulation becomes dramatic because of electron depletion in the entire crystallite, and results in higher sensitivity to gases. In 1991, Xu et al [16] demonstrated the dependence of sensitivity on grain size for a porous SnO₂ gas sensor. By using additives such as aluminium and antimony in the SnO₂ powders followed by sintering, they were able to control the SnO₂ grain size in the range of 5–32 nm. They demonstrated that the sensitivity was dependent on the size of the crystallite in the regions near Debye length. These previous studies demonstrate that control of the microstructure of SnO_2 in the nanometer range can significantly improve the performance of a chemical sensor.

More recent efforts to control the microstructure of SnO_2 have involved higher temperature oxidation of tin [17], doping SnO_2 with different metals as dopants [18, 19], grinding SnO_2 to nano-sized powder followed by sol-gel paste preparation and sintering [20], precipitation of SnO_2 from hydrolysed stannic acid solution [21, 22], spray pyrolysis of SnO_2 [23], chemical vapor deposition (CVD) of SnO_2 [24], sputter deposition of SnO_2 [25], and SnO_2 deposition using pulsed laser ablation [26] techniques. However, the conventional processing methods for making nanostructured SnO_2 films either from solid-state or wet chemistry are not readily compatible with the batch fabrication techniques employed for fabricating the CMOS (complementary metal–oxide– semiconductor) compatible microhotplates [3, 4] addressed in this paper.

In this paper, high-temperature metals such as iron, cobalt, and nickel, and relatively low-melting temperature metals such as copper and silver have been investigated as seed layers for the microstructural control of SnO_2 . These various metal seeds are used to modify the nucleation behaviour of the CVD SnO_2 which occurs on the bare silicon dioxide (SiO₂) microhotplate surface. Since SnO_2 deposition is from the gas phase through CVD, the top SiO_2 surface of the microhotplate will influence the nucleation, growth, and the microstructure of the SnO_2 films. The nanoparticle metal seeds were used in an effort to modify the growth process in a controllable way to achieve smaller grained and more uniform SnO2 microstructures. Furthermore, all the steps in this method are easily reproducible, and we demonstrate the repeatability of seeded film growth by redundant fabrications with multi- element arrays.

The primary objective of this paper is to investigate the use of microhotplates to synthesize nanoparticles, using a seed-layer approach to form a range of devices for selective gas identification. The effects of nanoparticle seeding on the growth and microstructure of SnO_2 is presented, together with a discussion of gas sensitivity of nanoparticle-seeded SnO_2 to illustrate the benefits of nanostructured SnO_2 in terms of higher sensitivity in reducing gases. Detailed analysis of gas- sensing properties such as sensitivity, stability and selectivity is reported elsewhere [27, 28].

2. Microhotplate technology

A micrograph and schematic of a microhotplate gas sensor platform developed at NIST are shown in figure 1 [3,4]. These micromachined devices have lateral dimensions of ~200 μ m and are suspended over a cavity for thermal isolation. The physical architecture of each microhotplate consists of a heater, a thermometer plate and contacts. The polysilicon heater in the microhotplate is sandwiched between underlying and overlying SiO₂ layers. A metal hotplate layer is employed over the SiO₂ layer for temperature measurement and heat distribution. There are four contacts on the top SiO₂ layer of the microhotplate that are used to measure the conductance of the film during SnO₂ deposition and gas sensing. Each SiO₂ film layer serves to electrically isolate the conductive layers (heater, thermometer plate, contacts and sensing film). The suspended microbridge structure is realized by

anisotropic wet-chemical etching with ethylene diamine and pyrocatechol in water at 90 °C of the base silicon through the patterned open areas. The etching is selfterminated at the point of intersection of the {110} crystallographic planes with the {111} planes. This defines a cavity, which isolates the microhotplate from its surroundings. Depending on the design configuration and materials used, the microhotplates can operate anywhere from 20 up to 1000 °C. With aluminium as the thermometer plate, the microhotplates can operate up to 550 °C. With poly-Si, the microhotplates can operate up to 800 °C, and with tungsten, the microhotplate can operate up to 1000 °C. The thermal response time of the aluminium microhotplates from transient temperature measurements was found to be 0.6 ms [4]. The thermal efficiency or temperature/power coefficient in air is 8 °C mW⁻¹ [4].

3. Experiment

The preparation of microhotplate arrays involved dicing of individual arrays of microhotplates from the wafer, anisotropic etching of silicon to suspend the devices over their etched cavities, packaging, physical vapor deposition i.e. evaporation or sputtering of metallic seed-layer templates, and wire bonding.

The microhotplate wafers were fabricated at MIT-Lincoln Laboratories and MRL CMOS foundries. Once the wafers were received from the CMOS foundry, they were spin coated with photoresist before dicing. After the wafers were diced, the devices were etched using a prepared solution of ethylene diamine and pyrocatechol in water (EDP). After etching for 90 min, the {111} family of planes was exposed down to their common intersection wherein the (100) bottom plane disappeared, creating a pyramidal cavity as shown in figure 1. Once the etching was completed, the devices were rinsed in de-ionized water for 4–6 h to remove all the reaction products from the surface. The devices were then dried and were ready to be packaged.

Packaging of the 36-element arrays of microhotplates was done in an 84-pin ceramic package. The chips were mounted in the package using extra-fast-setting epoxy. Following packaging, the seed layers were selectively vapor deposited through a steel shadow mask. The shadow mask was 3 cm long and 2 cm wide. A 2 $cm \times 500 \mu m$ hole was cut in the centre of the steel mask to expose a column of six microhotplates in the 36 × 36-element array. The mask was aligned to expose only the desired microhotplates using an optical microscope. The mask was secured to the chip package using a vacuum-rated tape and mounted in the evaporator chamber. Vapor deposition of metals was performed using a vacuum evaporator. Iron (~99.998%), nickel (~99.994%), cobalt (~99.9965%), silver (~99.9985%) and copper (~99.9985%) were obtained from Alfa Aesar as 0.25 mm diameter wire for use as seed layers. The chamber pressure was maintained at 1×10^{-7} Torr for 1 h before vapor deposition to minimize contamination during evaporation. The chamber pressure during metal deposition was 1×10⁻⁶ Torr. Each column of the 36element array, consisting of six microhotplates, was dosed with a different seed layer. The order of dosing is indicated in figure 2. Approximately 16 Å of coverage,

as measured by a calibrated quartz crystal monitor, was used for all the different types of seed layers. The rate of seed-layer deposition was maintained at 0.1 Å s⁻¹ for all the different seed-layer metals. Following vapor deposition, the evaporator was allowed to cool and the chamber was brought back to atmospheric pressure. The sample was removed from the chamber, and the mask was re-positioned using an optical microscope to expose a different column of microelements. This process was repeated to obtain a total of five different metals on five different columns of the 36-element array. One of the columns was not dosed with any metal so that those elements could be used to observe the growth, and microstructure of SnO₂ on unseeded microhotplates, and provide a basis of comparison for the seeded growth.

3.2. Self-lithographic CVD of SnO₂

After seed-layer deposition on 30 of the 36 array elements, the chips were placed in the CVD reactor for SnO₂ deposition. A schematic of the metal–organic chemical vapor deposition system (MOCVD) is shown in figure 3.The system consisted of a chamber with a socket where the packaged and wire-bonded chips were mounted. Electrical connections to the socket were made through a vacuum feedthrough such that each microhotplate was individually addressable electronically. Ultrahigh purity argon (~99.9999%) and oxygen (~99.9999%) were used as the carrier and the reactant

gases, respectively. The flows of oxygen and argon were regulated using mass-flow controllers. Tetramethyltin (purity level ~99.99%), used as the metal source for SnO_2 deposition, was placed inside a stainless steel bubbler. To attain a desirable vapor pressure or gas phase concentration the source was kept inside a methanol bath whose temperature was maintained at -40 °C. Deposition occurred by thermally activated decomposition of tetramethyltin on the localized heated area of a particular microhotplate substrate. Since no external lithographic steps were required to pattern the film on the suspended device, the deposition may also be described as a 'self-lithographic' CVD process [4,5,29]. The conditions for SnO_2 deposition used for all the seeded and unseeded elements are given in table 1.

SnO₂ was deposited sequentially on each of the microhotplate in the 36-element array. The electrical conductance of SnO₂ during deposition was monitored using contact pads on the microhotplates, and the growth or microheater was shut down once the conductance reached $2 \times 10^{-4} \Omega^{-1}$. The conductance was monitored on each microhotplate using contact pads that are located directly opposite to each other and are 29 µm apart (as shown in figure 2). It has been observed from prior experience that SnO₂ films grown to this conductance level show favorable favorable gas-sensing properties [11]. Appreciable changes in surface conductance are needed in thin-film gas sensing; films grown to lower conductance (<1 × 10⁻⁶ Ω^{-1}) may not be continuous enough to give an appreciable change in film conductance during gas sensing, whereas films grown to higher conductance (>1 × 10⁻³ Ω^{-1}) are thicker and show bulk properties, rather than surface sensitivity. It

should be emphasized that conductance of films was monitored during growth and not thickness. Direct film thickness measurements on microhotplates are difficult due to their suspended structure and small geometry. The control of electrical properties of SnO_2 films is used as the basis for growth in this study, due to the end use of these devices as conductometric gas sensors.

3.3. SEM characterization

Microstructural characterization was carried out in a Hitachi S- 4700 field emission scanning electron microscope. Operating voltages used to image the SnO₂ films on the microhotplate arrays were between 0.5 and 30 keV. One of the advantages of using arrays is that information about the microstructures of a variety of samples may be obtained in a single SEM session, avoiding the contamination of specimens during multiple loadings and unloadings. Using the single-loading approach, each element of the array was carefully investigated and the microstructures were compared. Reproducibility of microstructures from elements in a single- array column, consisting of similarly processed SnO₂ was examined. Furthermore, to investigate the reproducibility and microstructural control of the seed-layer method for films grown on different microhotplate chips, samples of pure SnO₂ and nickel-seeded SnO₂ were also prepared on four- element arrays. SEM images were subsequently captured and compared to the pure SnO₂ and nickel-seeded SnO₂ from the 36-element array.

Following SEM characterization of microstructures, average grain sizes of both seeded and unseeded SnO2 microstructures were determined. Grain sizes were measured from the SEM images for three elements in a column in the 36-element array. One hundred measurements were made to calculate the average grain size for each of the three elements in a column. For simplicity, the grains were classified into two types. Those film microstructures whose grain sizes fell in the range of 50 nm or above were called coarse- grained microstructures, and those films whose grain sizes fell below 50 nm were called fine-grained microstructures. Statistical analysis of grain size distribution was performed to investigate the microstructural uniformity for each type of SnO₂ by column, as described above. Correlations between grain sizes and melting temperatures of the various seed metals was performed with the results leading to questions about the seed-layer structure and SnO₂ growth mechanisms. To answer these questions, SEM images were taken of asdeposited seed layers, and seed layers heated to 500 °C at 4.2 Torr in argon and oxygen using four-element arrays of microhotplates. The flow rate of argon and oxygen were the same as used for SnO2 deposition process. Two types of metals, namely nickel (high- melting temperature) and silver (low-melting temperature), were examined in detail due to the dramatic differences in SnO2 microstructure produced by these seed metals. 16 Å of each metal was vapor deposited selectively onto microhotplate elements. Following seed-layer deposition, two microhotplate elements in each of the four-element arrays were heated to 500 °C and SEM images of all the four elements were captured to reveal the structure of the as-deposited

and heated seed layers. The structure of SiO_2 was also imaged as a basis for examining the changes introduced by metal seeding.

3.4. Gas sensing

as sensing was carried out isothermally in a mixture of air and 90 ppm ethanol at 400 °C. The details of the sensing apparatus is reported elsewhere [27, 28]. Prior to sensing, the films were annealed in air at 400 °C for 1800 s. Conductance was monitored during the entire test period using the contact pads on the microhotplate. The sensitivity ratio is defined as the ratio of film conductance in gas (G_g) to that in air (G_a).

4. Results and discussion

4.1. Structure of top silicon dioxide surface

Prior to depositing the metal nanoparticle seeds or the SnO₂ sensing film, the SiO₂ surface of the microhotplate was examined using SEM, as it can play an important role in the nucleation and growth of unseeded SnO_2 . As shown in figure 1, the microhotplates consist of multi-layer stacks of SiO₂ with the heater and the thermometer plate sandwiched between the SiO₂ layers. Depending on the foundry and the fabrication process, the top layer SiO_2 can exhibit different film structures and can influence the SnO_2 growth and morphology. Two types of microhotplates fabricated at two different foundries were investigated during this study. Figure 4 shows scanning electron micrographs for the top SiO₂ surfaces from the two different types of microhotplates. The micrograph in figure 4(a) is the structure of chemo-mechanically polished SiO₂ surface fabricated at the MIT-Lincoln Laboratories, and the micrograph in figure 4(b) is the structure of SiO₂ from the microhotplate fabricated at MRL. Thermal oxidation of silicon was used in both the foundries for SiO₂ deposition. However, the SiO₂ surfaces from MIT-Lincoln Laboratories were chemo- mechanically polished to obtain a planar surface. It can be seen from figures 4(a) and (b) that the structure of SiO₂ provided by each foundry is quite different. It will be seen in the section on microstructure, that these different SiO₂ surfaces give rise to different pure SnO₂ film morphologies; however, similar SnO₂ morphologies were produced on both foundry types of microhotplates with nanoparticle seeding. These observations indicate the level of control and the minimization of substrate effects achievable through nanoparticle seeding.

4.2. Tin oxide growth and reproducibility

Figure 5 compares the conductance curves recorded during the growth of nanoparticle-seeded SnO_2 . Each curve represents the average growth data over six microhotplate elements of the same type. The growth process can be described as the onset of the nucleation of SnO_2 particles, and the growth of SnO_2 particles into a continuous film. It can be seen in figure 5 that each type of metal seed layer has a different time for the onset of film conductance, also known as the induction time to

continuity. Although SnO₂ might start nucleating much earlier, a change in electrical conductance is only observed after the film becomes continuous or an electrical path between the contacts is established. Measuring the capabilities of the instrument is also important since the change in conductance is only observed after the conductance of the film reaches the measuring capability of the instrument. The maximum resistance that can be monitored using the Keithley 2001 digital multimeter is 1 G Ω . The nanoparticle-seeded SnO₂ films on microhotplates reached the selected shut down conductance faster than for the films grown on microhotplates, the SnO₂ films on the microhotplates with iron seeding reached the shut down conductance in the shortest time, followed by the films grown on cobalt, nickel-, silver- and copper-seeded microhotplates, respectively. The observed dependence of growth rate on the type of nanoparticle seed suggests varied nucleation effects produced by the different metals during SnO₂ growth.

The longer growth times for the unseeded SnO₂ could be due to the poor sticking coefficient of tetramethyltin on SiO₂ . Studies on the wettability of polished SiO₂ layers have indicated that the adhesion and the contact angle hysteresis decrease with increasing temperatures of between 50 and 300 °C [30]. It may be possible that the sticking coefficient of tetramethyltin on SiO₂ is even lower at 500 °C, the deposition temperature of SnO₂ , which could possibly explain the longer growth times observed for the unseeded SnO₂ (see figure 5 induction and shut-off time). The higher sticking coefficient of metals may improve the adhesion of tetramethyltin and aid the faster nucleation of SnO₂ , which may explain the observed faster growth times for the nanoparticle metal seeded microhotplates. It may also be possible that the metal seeds act as catalysts for the initial nucleation of SnO₂ in the CVD process. The catalytic action of nanoparticle metals during the initial CVD growth process needs to be further examined in detail and is beyond the scope of this study.

Figure 6 compares the conductance curves between unseeded- and nickel-seeded SnO₂ film grown on two different columns of the 36-element array chip. The curves also illustrate control and reproducibility of SnO₂ growth both for unseeded as well as nickel-seeded samples in a single chip. It can be observed that the growth parameters such as time to reach final shut-down conductance, and film resistance at room temperature are within ±10% of the mean, demonstrating good reproducibility of SnO₂ growth. Similar reproducibility was also observed for films formed with other seed layers on the same chip as well as on different chips for the same deposition conditions. To check reproducibility between substrates (fourelement arrays versus 36-element arrays), pure SnO₂, and nickel-seeded SnO₂ was grown on pairs of elements of a four-element array. Figure 7 compares the monitored growth conductance of nickel-seeded and unseeded SnO₂ from the fourelement array of microhotplates. Comparing figures 6 and 7, it can be seen that the time for the onset of continuous growth, and the time to reach final shut-down conductance were approximately the same for nickel-seeded SnO_2 sensors on both four- and 36-element arrays. This result illustrates the reproducibility and control of the SnO₂ seed-layer growth process when it is independently carried out on separate microplatforms. Comparing the growth of unseeded SnO₂ between figures 6 and 7, although good reproducibility was obtained for the elements within each type of microplatform, dramatic differences in growth can be observed between the different micro-arrays under the same growth conditions. This difference in growth between the arrays when seeding is not employed could be due to substrate effects, which lead to irreproducibility of the microstructure and final sensing properties between different arrays. The observed substrate- induced effects could be due to various factors, including variations in post-CMOS processing (such as EDP etching), rinsing after etching, process-induced defects on the SiO₂ such as pinholes and hairline cracks during SiO₂ deposition), and chemo-mechanical polishing. Each of these could affect the surface characteristics such as adhesion of the SiO₂ and in turn affect the nucleation and growth process of SnO₂.

4.3. Tin oxide microstructure and reproducibility

Microstructural characterization has revealed the level of control that nanoparticle seeding can impart on the microstructure of SnO_2 films. Figures 8(a) through (f) present the various SnO₂ microstructures produced by the different types of nanoparticle seeding. The same deposition temperature and pressure was maintained for SnO_2 deposition on different nanoparticle seed layers. The micrographs show that while qualitative similarities exist between certain types of films, each type of seed metal produced a quantitatively unique SnO_2 morphology. Significant differences in microstructure were observed for these microhotplatebased films. Copper- and silver-seeded SnO₂ films showed morphologies that markedly differed from the other films. The qualitative morphological similarities between iron-, cobalt-, and nickel- seeded SnO₂ films correlate well with the similar slopes of growth conductance in figure 5. Although the morphologies of iron-, nickel-, and cobalt-seeded SnO₂ films were qualitatively similar, the grain sizes for these films differed. Table 2 gives the mean grain size, and standard deviation for each type of SnO₂. The SEM images revealed a fine-grained microstructure for iron-, nickel- and cobalt-seeded films and coarse-grained structure for silver-, and copperseeded, and unseeded SnO2 films.

As a reproducibility check, SEM images of three elements from a column of pure SnO_2 , and nickel-seeded SnO_2 from a 36-element array are presented in figures 9(a) and (b). The similarity of all the three elements of each type illustrate the degree of microstructural reproducibility that results from the unseeded and the nickel nanoparticle seeding. Similar reproducibility was achieved for the other nanoparticle-seeded SnO_2 films.

Figures 10(a) and (b) are the SEM images of pure SnO_2 and nickel-seeded SnO_2 grown on a 4-element array. Comparing figures 10(a) and 9(a), it can be seen that differences in grain size exist for the pure SnO_2 films grown using a 36- and fourelement array. This morphological evidence correlates well with the conductance growth differences observed for unseeded films on four- and 36- element arrays (see figure 7). Grain size analysis of unseeded SnO_2 revealed grain sizes of ~75 nm on a 36-element array, and ~480 nm on a four-element array. Although both the 36and four-element arrays came from the same wafer, back-end processes such as etching could have altered the surface characteristics of SiO_2 , contributing to the observed differences in the pure SnO_2 growth between these substrates. However, the nickel-seeded SnO_2 films look similar for both substrates (figures 9(b) and 10(b); this further illustrates the controllability of SnO₂ film growth that nanoparticle seeding can introduce (see also figure 6). In fact, grain size analysis revealed the same average grain size of \sim 38 nm for the nickel- seeded SnO₂ on both arrays. As already mentioned, the top-surface SiO_2 of the microhotplate can affect the nucleation and morphology of SnO₂ films. To explore this issue further, SEM investigations were performed on pure SnO₂ films as well as nanoparticle- seeded SnO₂ films grown from microhotplate devices from two different foundries. Figure 4 illustrates the different surface morphologies of SiO_2 fabricated at the two foundries. The chemo-mechanically-polished SiO₂ fabricated at the MIT- Lincoln Laboratories has a surface that is planar, whilst the SiO₂ fabricated at MRL has a non-planar surface. Figure 11 presents SEM images of pure SnO₂ and nickel-nanoparticle SnO₂ films grown on the two different SiO₂ surfaces from different foundries. It can be seen that the morphology of pure unseeded SnO_2 films (figures 11(a) and (c)) look quite different, while the morphology of nickel nanoparticle-seeded SnO₂ films (figures 11(b) and (d)) look quite similar. Since the SnO_2 was deposited on the SiO_2 surface as well as contact pads on the microhotplate device, SEM investigations were performed to reveal any differences in the microstructure of the SnO_2 that grew on these two different surfaces and is shown in figure 12. It can be seen that the pure SnO_2 morphologies on the contact pads (figures 12(a) and (c)) look different, while those of nickel-nanoparticle-seeded SnO₂ films (figures 12(b) and (d)) look similar, again illustrating the level of control achievable through nanoparticle engineering.

4.4. Correlation between growth conductance and microstructure

The growth and the microstructure of SnO_2 -sensing films were investigated in the previous sections, and the level of control of growth parameters and grain size using seeding was illustrated. In general, the iron-, cobalt- and nickel-seeded SnO_2 films showed similar growth and microstructure compared to the other types of SnO_2 films. This may be due to similar nucleation effects produced by these seed metals during SnO_2 growth. A correlation between change in growth conductance per time and grain size would help to understand the similarities or differences between different seeds. Figure 13 is a plot of the change in conductance per time versus the SnO_2 grain size. It can be seen that a higher level of changes in conductance per time was associated with a smaller SnO_2 growth and a produced smaller grain size. These facts show that these metals (Fe, Co, and Ni) are good choices as seed layers for obtaining smaller SnO_2 grains.

4.5. Statistical analysis of grain size distribution

More detailed analyses of grain-size distributions were performed on 100 grain measurements so as to produce histograms for each type of SnO₂. The spread in grain size over the measured values can be fitted by a Gaussian curve. Steeper slopes in the Gaussian fits are indicative of a more uniform grain-size distribution over a narrow range. Figures 14(a) through (f) present the statistically analysed data on grain size distribution. The figures indicate uniform grain size for iron-, cobalt- and nickel-seeded SnO₂ films. The distribution is spread out with more gentle slopes in the Gaussian fit for copper- and silver-seeded films in addition to the unseeded SnO_2 films. This large distribution in grain size for these three types of films indicate two or more competing growth processes of SnO₂ growth. Narrow grain-size distribution or uniformity of microstructure is preferred in the sensing applications of SnO_2 , since they generally provide more predictable and reproducible results. Non-uniformity of the microstructure can result in an irreproducibility of the sensing behaviour from one sensor to another, and thus should be avoided. The narrow grain-size distribution obtained for iron-, cobalt- and nickel-seeded films suggests that these metals are good choices as seed layers for the microstructural control of SnO₂ for chemical microsensor applications.

4.6. The structure of the nanoparticle seed layer and growth mechanism of seeded SnO_2

The nature of the metal seed strongly influences the final morphology of the SnO_2 film. This influence may be in part due to the different melting temperatures of the metal nanoparticles. Figure 15 is plot of the average SnO_2 grain size versus the melting temperature of the seed-layer metal. It is seen that seed-layer metals with high-melting temperatures produced smaller SnO_2 grain structures compared to metals with low-melting temperature. A linear fit through these measurements suggests a relationship between the melting temperature Tmelt and the grain size given by

 $D = -0.12T_{melt} + 207.82$

where T_{melt} is the melting temperature in °C, and D is the grain size. Good correlation between the seed-layer melting temperature and the final SnO₂ grain size suggest possible localized melting or surface diffusion of seeds in the initial processing that occurs before SnO₂ nucleation and growth. SEM investigations were therefore employed to explore the initial morphology of high-melting-temperature (nickel) and low-melting-temperature (silver) seed layers.

SEM investigations of nickel and silver seed layers revealed dramatic differences between the as-deposited and heated seed layers for these metals. The amorphous seed layers were heated in the CVD chamber to 500 °C, which was the same as the deposition temperature of SnO_2 . The atmospheres (including monitored oxygen and argon flows) were the same as those employed during the SnO_2 deposition process; however, tetramethyl-tin was not used in the chamber. The as-deposited films were

continuous for both nickel and silver seed layers as shown in figures 16(a) and (c), respectively. On heating, the nickel and silver continuous films were both observed to break into nanoparticle clusters as shown in figures 16(b) and (d), respectively. The mean size of the nickel particles produced by the annealing was found to be \sim 21 nm, and that of the silver particles was found to be \sim 60 nm. Histograms for the particle size distributions of nickel and silver nanoparticles were measured and plotted. The histograms in figure 16 shows a narrow-particle size distribution for the nickel nanoparticles and a bimodal-particle distribution for the silver nanoparticles. The silver particles ranged in size from 40 to 70 nm. The microstructure and the statistical distribution of the nickel and silver nanoparticles are consistent with their respective SnO_2 grain structures in the films grown on them. The narrow-particle size distribution of the nickel seed layer (figure 16(b)) was correlated to the narrow-grain size distribution of the nickel-seeded SnO2 (figure 8(b)). Similarly, the bimodal-particle distribution of the silver seed layer (figure 16(d)) was correlated with the bimodal grain size distribution of the silverseeded SnO_2 (figure 8(f)). These correlations indicate that the morphology of the seed layer is well preserved in the SnO_2 microstructure and the growth of SnO_2 on top of the seed layer can be viewed as an encapsulation process of the seed layer. The initial morphology of the seed-layer clusters produced during the initial heating dictates the final SnO_2 grain structure produced in the CVD deposition process. The initial seed-layer films, which were continuous, were observed to break into particle clusters on heating, and were defined as the varied templates for the SnO₂ growth. Heating the seed layers provides enough thermal energy for the seed layers to arrange themselves into distinct islands on the SiO₂ substrate as shown in figures 16(b) and (d). The differences observed in the particle size between the nickel and silver seed layers were believed to be due to their different melting temperatures giving rise to different levels of particle coarsening during heating.

4.7. Gas sensitivity

Figure 17 presents the plot of the sensitivity ratio versus the SnO_2 grain size for the different types of nanoparticle seeded SnO_2 films from the 36-element array. The sensitivity ratio is defined as the ratio of film conductance in gas to that in air. Each data point presents the average sensitivity values from six identical sensors from a single microhotplate array. The error bars represent the standard deviations from the average sensitivity values. Figure 17 illustrates the increase in sensitivity is believed to be due to the increase for 90 ppm ethanol. The increase in sensitivity is believed to be due to the increase in surface area of the grain boundary sensing sites due to the grain diameter decreasing. These results illustrate the benefits of nanoparticle SnO_2 for chemical microsensor applications using the seed-layer approach. Detailed sensing performance parameters such as sensitivity, stability, and selectivity of nanoparticle-seeded SnO_2 in various gases are reported elsewhere [27, 28].

5. Conclusions

The use of selected metals as nanoparticle seed layers to control the growth and microstructure of SnO₂ films on microhotplate devices with SiO₂ surfaces has been investigated. This study took advantage of the efficiency provided by the array-based microhotplate platforms. High temperature metals such as iron, nickel and cobalt, and relatively low melting temperature metals such as copper and silver were investigated as seed layers. Using 90 ppm ethanol as a test case, seeding with high-temperature metals such as nickel, iron and cobalt resulted in faster SnO₂ growth, smaller SnO₂ grain size and higher sensitivity. Furthermore, seeding was found to eliminate the effects of substrate morphology on the SnO₂ microstructure. Seeding with nickel on two different SiO₂ substrates (CMP polished versus unpolished) resulted in similar a SnO₂ morphology on both surfaces.

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Figure 1. (a) SEM image of a microhotplate suspended in a cavity with contact electrodes on top, (b) schematic of the multi-layered structure of a surface micromachined microhotplate.



Figure 2. Optical micrograph of a 36-element array showing the different seed-layer dosing in each column.



Figure 3. Schematic of the CVD system for growing SnO_2 films.



1.00 µm

Figure 4. (a) Structure of a chemo-mechanically polished SiO2 surface, (b) structure of an unpolished SiO₂ surface.



Figure 5. Effects of seeding on SnO_2 growth: electrical conductance growth comparison for the different nanoparticle-seeded SnO_2 films.



Figure 6. Comparison of the growth of nickel-seeded and unseeded SnO_2 as measured by film electrical conductance: grown using a 36-element array of microhotplates.



Figure 7. Comparison of the growth nickel-seeded and unseeded SnO_2 as measured by film electrical conductance: grown using a four-element array of microhotplates.



Figure 8. Effects of seeding on SnO_2 morphology: SEM images of (a) unseeded SnO_2 ; (b) nickel-seeded SnO_2 ; (c) cobalt-seeded SnO_2 ; (d) iron-seeded SnO_2 ; (e) copper-seeded SnO_2 ; (f) silver-seeded SnO_2 .



Figure 9. Microstructural control using nanoparticle seeding: representative micrographs from three elements in a column of (a) pure SnO2 and (b) nickel-seeded SnO₂.



Figure 10. Microstructure of SnO_2 grown using a four-element array of microhotplates: (a) SEM image of pure SnO_2 ; (b) SEM image of nickel-seeded SnO_2 .



1.00 µm

1.00 µm

Figure 11. (a) Structure of pure SnO_2 grown on a chemo-mechanically polished SiO_2 surface; (b) structure of nickel nanoparticle-seeded SnO_2 grown on a chemo-mechanically polished SiO_2 surface; (c) structure of pure SnO_2 grown on an unpolished SiO_2 surface; (d) structure of nickel nanoparticle-seeded SnO_2 grown on an unpolished SiO_2 surface.



Figure 12. (a) The structure of pure SnO_2 grown on the contact pads of the chemomechanically polished SiO_2 surface; (b) the structure of nickel-seeded SnO_2 grown on the contact pads of the chemo-mechanically polished SiO_2 surface; (c) the structure of pure SnO_2 grown on the contact pads of the unpolished SiO_2 surface; (d) structure of the nickel-seeded SnO_2 grown on the unpolished SiO_2 surface.



Figure 13. Correlation between rate of change of SnO_2 growth conductance versus SnO_2 grain size.



Figure 14. Statistical comparison of grain size distribution for (a) unseeded SnO_2 , (b) nickel-seeded SnO_2 , (c) cobalt-seeded SnO_2 , (d) iron-seeded SnO_2 , (e) copper-seeded SnO_2 , (f) silver-seeded SnO_2 .



Figure 15. Correlation between nanoparticle seed layer melting temperature and SnO_2 grain size, illustrating that high temperature melting metals are good choices as seed layers for microstructural control of SnO_2 films.



Figure 16. Morphology of nanoparticle seed layers: (a) as-deposited nickel seed layer, (b) nickel seed layer heated to 500 °C, (c) as-deposited silver seed layer, (d) silver seed layer heated to 500 °C.



Figure 17. Gas sensitivity of nanoparticle-seeded SnO_2 films as a function of grain size in 90 ppm ethanol.