Tin Oxide Cluster Assembled Films:
Morphology and Gas Sensors

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Abstract

In this thesis, investigations into fabricating tin oxide hydrogen gas sensors from films assembled by the deposition of tin clusters are reported. The tin clusters were formed in a UHV compatible cluster apparatus by DC magnetron sputtering and inert gas aggregation. Through SEM imaging, it was found that the morphology of tin cluster assembled films deposited onto silicon nitride substrates was highly coalesced. The coalescence between the clusters was significantly reduced by reacting the clusters with nitrogen before they were deposited. This resulted in granular films with a grain size close to that of the deposited clusters.

The coalesced and granular tin films were used to fabricate tin oxide conductimetric gas sensors. This was done by depositing the tin films onto gold contacts and then oxidising them by baking them at 250°C for 24 hours. The sensors were tested using a purpose built gas test rig. It was found that the sensors with the granular film morphology were much more sensitive to 500 ppm, 1000 ppm, and 5000 ppm of hydrogen at 200°C in ambient air with zero humidity. This was attributed to the smaller grain size and the larger surface area of the granular films.
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Chapter 1

Introduction

In this chapter, the background information and outline for the research presented in this thesis is given. There are four sections. The first two sections introduce the three major themes in this thesis, nanotechnology, atomic clusters, and gas sensors. The third section describes the previous work done at the University of Canterbury and its relevance to this thesis. The last section gives an outline on the work presented in the following chapters.

1.1 Nanotechnology

Nanotechnology is the study of the manipulation of matter on the molecular scale and promises to have a significant impact in many different fields. In the electronics industry, it provides the next step in the future miniaturisation of electronic devices and it will open up the possibility for the development of novel devices. In medicine, nanotechnology may lead to better drug delivery systems [1] and imaging techniques [2]. Nanotechnology is also expected to provide solutions to our increasing energy demands by leading to more efficient lighting [3], solar energy conversion [4], and energy storage [5].

One of the key aspects of nanotechnology is the study of the unique properties of nanomaterials. The nanoscale marks the point where materials are no longer in their bulk form; it is where quantum confinement and surface effects begin to be significant [6]. As a result, the properties of materials become size dependant and can differ dramatically from their bulk form. For instance, metals can become semiconductors [7] and the melting points of solids typically decrease with size [8].

The high surface to volume ratio of nanomaterials makes them particularly chemically active. For example, aluminium in bulk form is relatively inert, but on the nanoscale it becomes combustible [9]. This is the reason why many nanoparticles have been found to make very effective catalysts [10]. Nanomaterials can be used as very sensitive gas sensors because surface reactions dominate their electrical properties [11].
Many of the problems we face in nanotechnology today are related to harnessing these properties of nanomaterials and using them in workable devices. For instance, carbon nanotube transistors have been built that show promising performance [12]. However, there is no fast and easy way to control the placement of the carbon nanotubes to form dense complex circuits. In addition, the high surface to volume ratio of nanomaterials can also be a hindrance to the fabrication of devices as it increases the driving force behind diffusion, which can lead to unwanted coalescence between nanomaterials that are in close proximity.

1.1.1 Atomic clusters

Atomic clusters are aggregates of anywhere from two atoms up to millions of atoms [13] and are interesting for many reasons. They are nanosized, and so they have the unique properties described above. By increasing the size of clusters we can see how phenomena not seen in single atoms, such as electronic band structure and superconductivity, becomes present in bulk solids. Clusters display exotic properties. In many cases, the structures of clusters are found to be five-fold symmetric, which is not seen in bulk materials [14]. This is a result of the cluster reducing its large surface energy. Clusters have ‘magic numbers’, which correspond to the number of atoms that form the most stable clusters [15, 16].

There are many methods for producing clusters. They can be made chemically in solution [17]. Clusters can be removed directly from a solid surface using photon and heavy particle collisions [13]. They can be made by forming a vapour of atoms via heating, sputtering, or directly laser ablation of a solid target [18]. In this case, the atoms in the vapour will aggregate into clusters if their velocity is reduced sufficiently, which is the method used in this thesis. This can be achieved by using supersonic jets or inert cooling gases.

From an engineering perspective, clusters are of great interest because their properties are size dependent. In one experiment, the band gap of mercury clusters was shown to decrease as the number of atoms in the cluster increased from 3 to 250 [7]. At around 150 atoms, the band gaps closed and the clusters went from semiconducting to metallic. This size dependence opens up the possibility of tuning desired properties by altering the size of clusters. Currently most devices are made using the top-down approach, which involves the combination of lithography and etching to reach dimensions of around 10 nm [19]. The bottom up approach, of using clusters as building blocks for the assembly of devices, allows that nanoscale resolution to be achieved instantly [20].

1.2 Conductimetric gas sensors

In 1953, Brattain and Bardeen [21] discovered that the conductivity of a semiconductor changes when gas is absorbed on its surface. Since then, gas sensors based
on conductance measurements of semiconductors have been widely studied. In particular, much emphasis has been put on metal oxides because of their low cost, robustness, and their sensitivity to a large range of reductive and oxidative gases [22]. The principle mechanism for gas detection in metal oxides in ambient air is the ionosorption of oxygen at its surface, which produces a depletion layer (for n-type semiconductors), and hence reduces conductivity [23]. Here, ionosorption refers to the process where a species is absorbed and undergoes a delocalised charge transfer with the metal oxide. This can then be used to measure reducing and oxidising gases, as they will change the amount of ionosorbed oxygen, and therefore the conductivity of the metal oxide.

At higher temperatures the absorption and desorption rates of oxygen are faster, resulting in a greater response and a lower response time for the gas sensor. However, the physical properties of the metal oxides place an upper limit on the temperatures that can be used. If the temperature is too high, the stability and reliability of the sensors diminishes because of possible coalescence and structural changes [11]. Furthermore, as temperature increases, the charge-carrier concentration will increase and the Debye length will decrease, resulting in less sensitivity [22]. In most cases, the optimal temperature for metal oxide gas sensors is between 200°C and 500°C.

Many different metal oxides, in the form of thin and thick films, have been studied for use as conductimetric gas sensors. Much of today’s focus is on thin films because of their small size and low power consumption; these properties also open up the possibility of having an array of sensors [22]. Furthermore, thin films are more reproducible than their thick film counterparts because their production process is more automated and controllable [11]. There are two well-known ways for improving the gas sensing properties of these films. The first is to add noble metals for their catalytic activity and to dope the film, with many reports showing that it leads to better sensitivity and stability, e.g. [24, 25]. The second is to reduce grain size, which has been shown to increase sensitivity [26]. This is because the depletion layer caused by ionosorption has a greater effect on the conduction channel of the grain as the grain size decreases. Consequently, there is great interest in using nanoparticles in gas sensors, since they can be used to make films with very small grain sizes.

1.2.1 Tin oxide films

Tin oxide (SnO₂) has been the most widely studied material for metal oxide gas sensors because of its low cost and its high sensitivity to many different gases. It is a n-type semiconductor with a band gap of 3.6 eV. In its pure and non-stoichiometric form, it has been shown to be sensitive in the ppm range to a wide variety of hazardous and environmentally important gaseous species, including H₂, NH₃, NO₂, CO, H₂S, O₃ and SO₂ (see [22] for a comprehensive list). In many cases, the use of dopants such as Pt and Pd has been used to improve the sensitivity and response times to these gases, and to lower the working temperature of these devices [25, 27].
The reduction in grain size to improve sensitivity has been well studied for tin oxide. The first experiments in this direction were done by Yamazoe et al. [28], where they used porous sintered SnO$_2$ and showed that its sensitivity to 800 ppm of H$_2$ and CO at 573 K dramatically improves as the grain size goes below 10 nm. Ansari et al. [29] showed that with thick films of tin oxide nanoparticles the sensitivity to 300 ppm of H$_2$ increased by a factor of 25 when the particle size went from 50 nm to 20 nm. Lu et al. [27] showed that with nanosized tin oxide powders with particle sizes ranging for 5 nm to 120 nm, the sensitivity improved considerably when the particle size went below 20 nm.

By far the greatest challenge in the development of tin oxide gas sensors is to improve their selectivity to different gases. This has been done, with limited success, by adding different metals and metal oxides to the film. Galdikas et al. [24, 30] showed that the doping level of Cu on tin oxide thin films could be used to modify the films selectivity to H$_2$ and CO. Ansari et al. [31] found that thick films of tin oxide doped with MoO$_3$ was selective to H$_2$ and CO at 140°C and 240°C respectively. Niranjan et al. [32] showed that ruthenium doped tin oxide thin films were extremely selective to LPG when compared with H$_2$, NH$_3$, CO, and other hydrocarbons.

### 1.2.2 Nanomaterials

An alternative to using metal oxides in the form of thin and thick films for gas sensing is to use them in their nanocrystalline form. With their crystalline structure and high surface to volume ratio, they are expected to be more stable and sensitive than their thin film counterparts [11]. In addition, the ability to control their dimensionality enables the possibility of tuning their gas sensing properties. So far, there have been some promising results. Comini et al. [33] have synthesised tin oxide nanobelts using vapour phase deposition and have found their sensitivity to CO, NO$_2$, and ethanol to be comparable, if not better than, to what has been found for thin and thick films. Jiaqiang et al. [34] prepared ZnO nanorods between 40 to 80 nm by a hydrothermal process. Theses were shown to be very sensitive to a range of 10ppm to 2000ppm of ethanol at 330°C in ambient air, and the response times were in the order of seconds. In a paper by Wang et al. [35], it was found that ZnO nano-rods, which had diameters ranging between 30 nm to 150 nm, were sensitive to 10 ppm to 50 ppm of hydrogen in air at room temperature. This sensitivity was then improved five fold by depositing Pd clusters onto the surface of the nanorods. The response times were in the order of tens of seconds.

A relatively new idea is to place the metal oxide nanowires into a field effect transistor (FET) configuration where the field is used to modulate the carrier concentration to improve sensitivity. Fan et al. [36] fabricated a FET consisting of a single ZnO nanowire on a SiO$_2$/Si substrate and a back gate. It was found that the nanowires sensitivity to oxygen was dependent on gate voltage. In another paper by the same group [37], a strong field was used to refresh the nano-wire FET gas...
sensors back to their original conductance. This is useful when the sensor is used at lower temperatures where the recovery times are slow.

1.3 Previous work at the University of Canterbury

The University of Canterbury has three systems for the production of atomic clusters, each of which uses an inert gas aggregation (IGA) source. The first of these systems is the high vacuum (HV) cluster apparatus, which was developed for electron diffraction experiments [38, 39, 40]. This system was also used to deposit clusters onto samples. However, it suffered from the fact that the high vacuum still resulted in water layer formation and the consequent oxidisation of samples [41]. The design also meant that only one sample could be made and characterised at a time. Furthermore, poor alignment and a narrow beam made characterisation difficult [42].

The other two systems are ultra high vacuum (UHV) compatible cluster apparatus’ and were designed to solve the problems of the HV system and to have more control in the production of clusters. This included the addition of a mass selection chamber. The difference between the two systems is the use of an evaporative source and a magnetron sputtering source. A detailed description of the UHV system can be found in the next chapter.

A number of experiments with a variety of cluster materials have been performed at the University of Canterbury. These have largely consisted of studying the properties of percolating films of clusters [43], finding means of producing cluster assembled nanowires [44], and using clusters for gas sensing [45]. Clusters made from antimony, bismuth, lead, silver, and tin have been studied to various degrees. For a complete review on these experiments see [46].

1.3.1 Tin oxide cluster films

Gas sensors based on tin oxide cluster films have been investigated by Lassesson et al [47]. The sensors were fabricated in the following manner. First tin clusters were produced using DC magnetron sputtering of a tin target in the UHV compatible cluster apparatus, then films of tin clusters were deposited between two lithographically defined gold contacts on Si/SiN substrates. The diameter of the clusters ranged between 3 nm and 10 nm. The sensors were then removed from the UHV into air resulting in partial oxidisation, and then fully oxidised by baking them at 200°C for 18 hours. It was found that there was very little coalescence between the deposited clusters. This resulted in a film morphology that was very granular with a grain size close to that of the deposited clusters (see figure 1.1a). Furthermore, it was also found that baking did not have a significant effect on the morphology of the films. It was concluded that the stoichiometry of the oxidised films was most probably SnO2.
Figure 1.1: SEM images showing the morphology of tin cluster films produced by the UHV compatible cluster apparatus (a) when there was a leak and (b) after the leak was fixed.

Figure 1.2: Resistance versus time for a film of tin oxide clusters exposed to varying concentration of (a) hydrogen at 80°C and (b) ammonia at 200°C.

Figure 1.2 shows the response of the tin oxide sensors to varying concentrations of hydrogen and ammonia in dry air at temperatures of 80°C and 200°C respectively. The sensors show a large reduction in resistance when exposed to these gases, however the response times were relatively long. By doping the films with Pd the response times were dramatically shortened and the sensitivity was improved. The performance of these gas sensors is very good compared to many other tin oxide films, and the low operating temperature is a desirable feature as it means the sensors could be used in low power applications. The good gas sensing properties of these samples is attributed to their high surface to volume ratio and small grain size.

The properties of tin oxide cluster films was further studied by Boyd et al [48]. In particular, emphasis was placed on the effect that baking had on the morphology and stoichiometry of the films. In these experiments, the tin films were produced in the same manner as the gas sensors but the baking procedure of the tin films was modified to 250°C for 24 hrs. Transmission Electron Microscope (TEM) images
showed that baking the clusters had little effect on the size and coalescence of the clusters. The optical transmission of the films was found to be greater than 90% for wavelengths from 700 nm to 380 nm, which is expected for SnO$_2$. Furthermore, it was shown that photo-desorption of oxygen dominates the photo-conductivity of the film which is also consistent with the films being polycrystalline SnO$_2$.

### 1.3.2 Tin oxide nanowires

A method for making and accurately positioning tin oxide cluster based nanowires on substrates has been developed by Boyd and Brown at the University of Canterbury [49]. Figure 1.3 shows a cross section SEM image of a nanowire sample and demonstrates the basic principle of the method. A Poly(Methyl methacrylate) (PMMA) bilayer is spun on top of a substrate and using electron beam lithography and lift off, a stencil like structure is formed. The undercut in the PMMA is due to the two layers of PMMA having different sensitivities to electron exposure. The width of the wire can be controlled by varying the electron dose on the PMMA, which in turn increases the width of the stencil. Tin clusters are produced using the UHV cluster apparatus and are then deposited onto the sample, where they pass through the stencil to form a nanowire on the substrate. After deposition the nanowire is exposed to air where it is partially oxidised. It is then fully oxidised into SnO$_2$ by baking it at 250°C for 24 hours.

The size dependence of tin oxide cluster nanowires configured as FETs was studied. This was done by making a four by four array of nanowires aligned between gold contacts on a Si/SiN substrate. The widths of the nanowires were varied between 60 nm to 130 nm. The conducting silicon substrate of the samples was used as the gate electrode and the 200nm SiN layer as the insulator forming a basic metal-
insulator-semiconductor FET (MISFET). It was shown that the nanowire based FETs behaved like n-type devices. It was found that the resistance of the wires decreased with wire width, and that the resistance of the smallest wire was much larger than the others. In addition, the gate voltage required for current pinch off increased with wire width. These two behaviours are a result of the surface depletion region on the nanowires having a more significant effect on the conduction channel in the wires as their width decreases. It was also found that the illumination of the nanowires with 365 nm UV light resulted in an increase in conduction by up to 40 times. This was thought to be mainly due to the photo-desorption of oxygen on the surface of the nanowires, increasing the carrier concentration in the wires. As this is a similar mechanism to how metal oxides are used for conductimetric gas sensors, it suggests that these nanowires could make good gas sensors themselves.

1.4 Thesis outline

The initial goal of this project was to make FET gas sensors from the highly sensitive tin oxide cluster assembled films described in the previous section. However, on first attempts to reproduce these films, we found that the deposited tin clusters coalesced to form films as seen in figure 1.1(b). It was discovered that a leak in the UHV cluster apparatus, that was fixed before the start of this project, was the reason behind the two distinct film morphologies. This lead to an investigation where nitrogen was deliberately added into the system, to see the effect it had on the coalescence of the clusters after they are deposited onto a substrate. In this study, we found a way to produce films with a similar morphology to that seen in figure 1.1(a). We then fabricated tin oxide gas sensors from the two distinct film morphologies and compared their response to hydrogen with the tin oxide cluster film gas sensors described in the previous section. In parallel to this, we intended to study the gas sensing properties of tin oxide cluster nanowire FETs described above. We could not do this with the time we had as the design of the nanowires meant that we would of have had to significantly modify the equipment used to test the sensors. However, we did manage to recharacterise the field effect of the nanowires and do some photo-conductivity experiments.

There are four subsequent chapters to this thesis. Chapter 2 discusses the experimental techniques used in this thesis, including a description of the equipment used throughout this thesis. The results of the nanowire measurements are presented at the end of this chapter. Chapter 3 presents the results of our characterisation of the UHV cluster apparatus, and the investigations on the film morphology and the effect of nitrogen on coalescence. Chapter 4 details the fabrication of the tin oxide sensors that were studied in this thesis; the results of the hydrogen gas tests on these sensors are presented. Chapter 5 concludes the thesis and discusses future possible work extending that presented here.
Chapter 2

Experimental techniques

In this chapter, a description of the systems and techniques used throughout this project is given. The first section discusses the design and preparation of the electrodes and the substrates that the tin clusters are deposited on to make sensors. The second section describes the UHV compatible cluster apparatus used to produce the tin clusters. The third and fourth sections give a brief description on how the tin samples were baked into tin oxide and how the samples were imaged. In the last section, the gas test rig that is used to test the gas sensors is discussed.

2.1 Sample design and preparation

Throughout this project, simple samples were used to make tin oxide cluster film gas sensors. These consisted of two large contact pads each connected to an electrode. The electrodes were approximately 0.5 mm wide and were separated by a 100 µm gap (see figure 2.1). The simplistic design was chosen because we expected that the electrode would not contribute significantly to the sensors resistance. This is because we expected a large number of grain boundaries with the cluster films, resulting in a negligible contribution to the resistance from the shottky contact between the electrode metal and the cluster film [50]. A gap size of 100 µm was chosen to give a reasonable resistance when the cluster film was deposited on the sample. Boron doped p-type silicon coated with a 100 nm LPCVD grown Si$_3$N$_4$ layer (Si/SiN) was used as the substrate because of its low current leakage.

The samples were made by clamping a shadow mask with the outline of 25 simple samples on top of a clean 4" Si/SiN wafer and then thermally evaporating the electrode metal onto the substrate. This was done inside an Edwards A306 thermal evaporator that had a base pressure of $10^{-6}$ Torr. To begin with, 5nm of Ni/Cr was deposited to assist the adhesion of gold on the surface of the substrate. Following this, 45nm of gold was deposited in order to form highly conductive contacts. The wafer was then broken into individual simple samples using a diamond-tip pen.

The substrate was cleaned both before and after the contacts were deposited.
This was done by first putting the simple samples in a solution of acetone and then by placing them in an ultrasonic water bath at 40°C for 4 minutes. This was repeated, replacing the acetone with isopropyl alcohol (IPA). Finally, the IPA was removed from the substrate using compressed nitrogen gas.

\section*{2.2 The ultra high vacuum compatible cluster apparatus}

Tin clusters were produced and deposited onto simple samples using a ultra high vacuum (UHV) compatible cluster apparatus built at the University of Canterbury \cite{51}. The system is designed to give reasonable control of the size distribution of the clusters produced, to have the capacity to mass select these clusters, to work in UHV in order to reduce the risk of unwanted reactions like oxidation, to be able to produce large cluster fluxes, and to have the flexibility to take samples in and out of the system easily.

The system consists of four stages as shown in figure 2.2. The first stage is the source, where the clusters are produced. The second stage is where the molecular beam of clusters is formed with the use of differential pumping and a skimmer. The third stage is the mass selection chamber. The fourth stage is where the clusters are deposited and where in situ electrical measurements on the clusters can then be made.

\subsection*{2.2.1 Stage 1: Magnetron sputtering and aggregation}

The tin clusters in the system are produced using a DC magnetron sputtering source in an argon atmosphere (see figure 2.3). Atoms are sputtered from a 99.99\% Sn target by bombarding the surface with argon plasma accelerated by an electric field.
This forms a vapour of tin atoms above the target and with the assistance of the argon gas the vapour is cooled and the atoms aggregate into clusters. The chamber where this aggregation occurs is cooled with liquid nitrogen in order to counteract the heat produced by the source and to assist aggregation. The discharge power of the magnetron sputter source can be varied; 15 W to 25 W is typically used for tin as higher powers result in the tin target melting. This has the effect of increasing the number of sputtered atoms and therefore changes the aggregation conditions. The aggregation length can also be varied from 0 cm to 25 cm, which in turn will have an effect on the growth distance and therefore on the formation of the clusters. In this project, we only used aggregation lengths between 0 cm and 13 cm as longer lengths required additional adjustment to the system. Another way to influence the formation of clusters is to vary the flow of argon, which is controlled using a MKS 117A mass flow controller. At times during this project nitrogen was added to the source chamber, as shown in figure 2.3, in order to study the effects it had on the morphology of the cluster films. The flow of nitrogen was controlled with another MKS 117A mass flow controller.
2.2.2 Stage 2: Cluster collimation

A beam of clusters is formed with the use of a nozzle, a skimmer, and with differential pumping. The clusters and the inert gas leave the aggregation chamber and are then accelerated through a nozzle (see figure 2.4) into a region of lower pressure, achieved with the use of a Pfeiffer roots pump. The gas then expands and is directed to the mass selection stage, which has been pumped down to an even lower pressure using a Pfeiffer turbo pump. A skimmer is used to sample from the expanding gas resulting in a collimated beam of clusters. The nozzle and skimmer are separated by a distance of 9 mm.

2.2.3 Stage 3: Mass selection and mass spectrum

The mass selection stage consists of a von Issendorff and Palmer mass filter [52]. For the purposes of this project mass selection was not required. However, the filter was used to find the mass spectrum of the clusters produced. Figure 2.5 shows the basic design of the mass filter. Clusters entering the mass selection chamber are partially ionized due to the sputtering process. The ionized beam enters the region between plates one and two, where a short high voltage pulse of time $t_p$ is applied to plate two and the clusters are accelerated perpendicular to their original direction. The ions then pass through a field free region between plates two and three and into the deceleration region between plates three and four. There, an identical but opposite high voltage pulse is applied at a time $t_d$ (delay time) after the first pulse was applied. The ions then lose their perpendicular velocity and continue through the exit aperture. The mass of the ions that are in line with the exit aperture.
depends on $t_p$ and $t_d$, since ions with different masses will reach the deceleration region at different times. Hence, by varying $t_p$ and $t_d$, the ionized clusters can be mass selected.

Simion simulations were carried out to find the optimum operating conditions for the mass filter by Ayesh [53]. In particular, it was found that a pulse height of 1400 V was needed in order to mass select the tin cluster sizes that were being produced by the magnetron sputter source. In the setup used for this project, the exit aperture was replaced by a Faraday cup. The signal strength measured by the Faraday cup is proportional to the number of mass selected ions, and therefore can be used in conjunction with the mass filter to measure the mass spectrum of the ionized beam. However, since the mass filter has a finite resolution, a range of masses ($\Delta m$) contribute to the measured signal. As an approximation we may write

$$Signal \propto N(m)\Delta m,$$

where $N(m)$ is the number of clusters with selected mass $m$. The theoretical mass resolution, $m/\Delta m$, of this mass filter is given, in [53], by

$$m/\Delta m = y/\Delta y \approx 12,$$

where $\Delta y$ is the height of the exit aperture and $y$ is the vertical distance between the centres of the entrance and exit apertures. As $\Delta y$ and $y$ are physical properties of the mass filter, the mass resolution is constant over the entire mass range. Therefore, $\Delta m$ is proportional to the selected mass, $m$, and we have that

$$Signal \propto N(m)\Delta m \propto N(m)m,$$

and so,

$$N(m) \propto Signal/m.$$
Figure 2.6: The dotted line shows a mass spectrum resulting from plotting the signal against the selected diameter. The solid line corresponds to the corrected mass spectrum where the signal has been divided by mass.

2.2.4 Stage 4: Deposition chamber

After passing through the mass selection chamber, the cluster beam enters the deposition chamber. This chamber can be isolated with the use of a pneumatically controlled gate-valve allowing samples to be removed and replaced without interrupting the rest of the system. The deposition chamber is pumped down to the lowest pressure out of all the stages using a Pfeiffer turbo pump. A cryostat cold finger is used to hold three samples, which can be moved vertically to place the samples in and out of the path of the beam (see figure 2.7). When the finger is fully retracted, a quartz crystal film thickness monitor is used to measure the cluster deposition rate, which is the thickness of atoms being deposited in a given amount of time. The deposition rate is used to estimate the thickness of material deposited on a substrate after a deposition. Throughout this thesis, the thickness of a film is either stated in nanometers or in monolayers of clusters (ML). A ML corresponds to a thickness equal to the average diameter of the deposited clusters.

The sample holders on the cryostat have gold plated contact pins that connect with the contact pads on the simple samples. These contact pins are connected to electrical feedthroughs out of the system that can be used to make electrical measurements on the samples. In this project, the conductivity of the simple samples
was monitored throughout the deposition in order to find if and when the samples become conducting, and how the conductivity develops as time goes on. This was done by applying a constant voltage of 50 mV to the samples and by using a Keithley 6514 electrometer and a Keithley 2000 multimeter to measure the current and voltage over the sample. The meters were connected to a computer and a labview program was used for data aquisition.

2.3 Baking

Tin oxide cluster films are made by depositing tin clusters onto a substrate in the UHV compatible cluster system and then oxidising them ex situ. This was done by baking them at 250°C for 24 hours with a Paragon SC-2 kiln.

2.4 Imaging

A Joel 7000F FE - SEM was used to image the samples in order to study the morphology of the tin oxide cluster films. All the images were taken with the accelerating voltage set to 15 kV.

2.5 The gas test rig

The conductimetric gas sensing properties of tin oxide films deposited on simple samples was studied using a purpose built gas test rig constructed at the University of Canterbury. The system is designed to provide controlled conditions and to
have the versatility to test the sensors with different gases and at different temperatures. The test rig consists of a chamber, where the sensor is held in a controlled environment, and the gas flow controllers, which control the chamber’s atmosphere by adjusting the flow of gas. Inside the chamber there is a heater and electrical feedthroughs which are used for conductivity measurements on the sensor.

2.5.1 Chamber design

The chamber consists of a sample holder (figure 2.8(a)) and stainless steel enclosing (figure 2.8(c)), which is kept airtight using an o-ring and four screws. The base of the sample holder contains a heater and a thermocouple. The sensor to be measured is placed between the base and a ceramic cap with gold plated contact pins that connect to the contact pads of the sensor. The contact pins are fed through to the outside of the chamber and are connected in order to make electrical measurements on the sensor. Pressure is applied to the ceramic cap using a central screw, as shown in figure 2.8(b), and an iridium heat shield is placed around the sample holder. The atmosphere in the chamber is controlled using a constant flow of gas through the chamber. The gas enters through the base of the sample holder (see figure 2.9) where it quickly fills the region around the sample, and eventually the rest of the chamber. The gas can leave the chamber at two exit points, one at the base of the sample holder, and the other in the outer region of the chamber, resulting in the chamber being held at approximately atmospheric pressure.

2.5.2 The heater and temperature control

A heater, immediately beneath the sample, is used to raise the samples temperature. The heater is a simple coil, which current runs through, creating heat because of the resistance of the wire. The current (which ranges from 0 to 20A) is provided by a HP 62598 DC power supply. The power supply is connected to an Omega CNi1654-DC temperature controller, which in turn, is connected to a thermocouple placed next to the heater. The temperature controller regulates the current supplied by the power supply in order to achieve a set temperature. The heater can be used to reach temperatures of up to 400°C.

2.5.3 Gas flow

Two MKS 117A mass flow controllers are used to regulate the flow of two gases into the chamber, and hence to control the chamber’s atmosphere. A MKS PR4000 controller is used to set the flow rate of each of the mass flow controllers. By varying the ratio of the two flow rates, the concentration of each gas entering into the chamber can be controlled.

In this project, we look to test the sensor’s response to hydrogen in similar conditions to what they will be used in commercial applications. For tin oxide gas sensors,
Figure 2.8: The gas test rig chamber at various points of construction: (a) First the ceramic cap is placed on top of the sample holder to make electrical contact with the sample; (b) then the heat shielding is placed around the sample holder and pressure is applied to the ceramic cap using a central screw; and (c) finally, the stainless steel enclosing is screwed to the base of the sample holder. An o-ring is used to make the chamber airtight.

this is normally in ambient air. Therefore, mixing air with the appropriate amounts of hydrogen, using the flow controllers, would give the most realistic conditions. However, it is well known that humidity plays a significant role in tin oxide sensors [54]. To remove this additional variable, we initially used dry air, with the intention of considering the effect of humidity later on. Consequently, one flow controller is connected to dry air and the other flow controller is connected to forming gas, which consists of 5% hydrogen in an argon balance. These two gases are mixed, and the hydrogen content of the air can be varied by changing the flow rate of each gas into the chamber.

In general, the total flow rate of the two gases was kept constant at 100 sccm. This was done because changing the flow rate was found to have a relatively large effect on the resistance of the tin oxide cluster film samples (see figure 2.10). This is thought to be caused by either the backflow of gases from the exit valve, humidity effects, the cooling of the substrate from the flow of gas, or by a combination of these.

2.5.4 Electrical measurements and the Labview interface

The resistance of a sensor in the gas test rig was monitored with the following set up. A Keithly 6487 Picometer/Voltage source was used to apply a constant voltage across the sensor. The current through the sensor was then measured using the
same meter and the voltage across the sensor was measured using a Keithly 2000 multimeter. The meters were connected to a computer via a GPIB interface and a Labview program was used to record the data from these meters. The Labview program was also used to remotely set the source voltage and the flow rates of the flow controllers. The program could be programmed to do this on a timed basis while recording the data from the meters; this allowed us to automate a specific cycle for the sensors to go through.

2.6 Parameter analyser and transistor measurements

The characteristics of the tin oxide cluster nanowire FETs described in section 1.2.3 were remeasured, and some further experiments with UV illumination were done. The results are presented in this section. The measurements were made using a Hewlett packard 4155A semiconductor parameter analyzer (SPA) combined with a Model 1800 micromanipulator probe station. The SPA has four source-monitor units (SMU), which can be programmed to be either a constant or variable voltage source, a constant or variable current source, or a ground connection. The SMUs
Figure 2.10: The effect of the flow rate of dry air on the resistance of two tin oxide cluster sensors, tfw68 and tfw69, at 300°C. The y-axis shows the resistance at that flow rate divided by the resistance at a flow rate of 100 sccm. The details of these sensors can be found in section 4.1.

are connected to a device via the probe station, which with the use of a microscope, can be used to accurately place probes to make contact with the device. The current and voltage was measured with various monitors within the analyzer.

2.6.1 Tin oxide cluster nanowires

The tin oxide cluster nanowires are made in a four by four array on a single Si/SiN substrate. The columns are labelled with the letters A, B, C and D, and the rows are labelled with the numbers 1, 2, 3, and 4. Each row of nanowires has been made with approximately the same width. Many of these nanowires were not conductive after deposition and some of them have broken since. Table 2.1 shows the width and resistance of the nanowires that are still conductive. The width of the wires was measured by taking SEM images [49], and the resistance was calculated from the slope of the I(V) curves measured for each wire. A general trend can be seen where the resistance decreases with wire width, this is consistent with [49].

2.6.2 Transfer characteristics

Figure 2.11 shows how the nanowires are configured into a simple MISFET. The conductive p-doped silicon act as the gate electrode, the SiN acts as an insulator, and the metal contacts acts as the drain and source electrodes. Figure 2.12 shows the transfer characteristics of the FETs measured using the SPA. These were found by applying a constant drain-source voltage (Vds) and measuring the resulting drain-source current (Ids), while the gate voltage (Vgs) was swept from -20 V to +30 V. This was done for a drain-source voltage ranging form 1 V to 5 V. Again the results
Table 2.1: The width and resistance of the tin oxide cluster nanowires that are still conductive.

<table>
<thead>
<tr>
<th>Nanowire</th>
<th>Width (nm)</th>
<th>Resistance (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>130</td>
<td>3.1</td>
</tr>
<tr>
<td>A2</td>
<td>90</td>
<td>260</td>
</tr>
<tr>
<td>B1</td>
<td>130</td>
<td>6.4</td>
</tr>
<tr>
<td>B3</td>
<td>70</td>
<td>1200</td>
</tr>
<tr>
<td>C1</td>
<td>130</td>
<td>55</td>
</tr>
<tr>
<td>C2</td>
<td>90</td>
<td>450</td>
</tr>
</tbody>
</table>

Figure 2.11: A nanowire configured as a simple MISFET device.

shown here concur with those found in [49]. The transistors behave like n-type devices; a negative gate voltage depletes the nanowire and reduces the drain-source current. Furthermore, the field effect becomes stronger as the width of the nanowires decreases.

2.6.3 UV experiments

The effect of the gate voltage on the photo-conductivity of the A2 nanowire was studied. A constant voltage of 1 V was applied between the source and drain of the nanowire and the current was monitored over time. Around three minutes was needed before the current reached a steady value. The wire was then exposed to 365 nm UV light for around 30 minutes and then allowed to reach a steady value again. This was done for constant gate voltages of -30 V, 0 V, and 10 V; figure 2.13 shows the results of this experiment. For each gate voltage, when the UV light is turned on, the current increases until it is saturated. For a gate voltage of -10 V and 30 V, the current returns back to its original value after illumination has stopped. However for a gate voltage of 0 V, the current drops slightly and becomes very noisy. This behaviour may have been due to some kind of change in the wire - it was the last measurement of the three gate voltages.

As explained by Boyd and Brown [49], the increase in current is due to the desorption of oxygen at the surface of the wire when it is illuminated with UV light. This causes the depletion layer of the wire to decrease in width, and therefore
Figure 2.12: The transfer characteristics of SnO$_2$ nanowires (a) A1, (b) A2, (c) B1, (d) B3, (e) C1, and (f) C2, configured as FETs. Plot shows Ids vs Vgs for Vds increasing from 1 V (lowest curve) to 5 V (highest curve) in 1 V steps.

causes the conductivity to increase. When the UV light is turned off, the oxygen is reabsorbed, and the wire returns to its original resistance. The effect of the gate voltage does not appear to be that significant. However, if we define the response as the saturated current during illumination divided by the initial current, then we do see that the response increases as the gate voltage goes from positive to negative. Further measurements need to be done to confirm this.
Figure 2.13: The source-drain current of the A2 nanowire as it is exposed to 365 nm UV light for 30 minutes, where a constant voltage of (a) -30 V, (b) 0 V, and (c) 10 V has been applied across the gate electrode. A constant voltage of 1 V was applied across the source and drain.
Chapter 3

Tin clusters and film morphology

This chapter consists of two main sections. The first section discusses the effect the source conditions have on the production of clusters in the UHV compatible cluster apparatus. The second section is a study on the morphology of the films produced by depositing clusters on Si/SiN substrates in the UHV system. In particular, a comparison between films made with and without the addition of nitrogen into the source chamber is made.

3.1 The characterisation of the source

The effect the aggregation length, the flow rate of argon, and the discharge power has on the deposition rate and the size distribution of the tin clusters was studied using the film thickness monitor and the mass filter. In particular, the aim was to find the conditions where there was a good deposition rate to produce samples in the quickest time possible. Furthermore, we needed to know how the source conditions affect the mass distribution of the clusters. This was important for making reproducible depositions because the mass spectrum can change from day to day even though the source conditions are kept constant. The range of parameters that we could study was limited by the fact that a deposition rate below 0.04 Å/s did not give a clear mass spectrum. These results corresponds to when there was no leak in the system.

3.1.1 The deposition rate

The deposition rate as a function of the aggregation length and the argon flow rate for a discharge power of 20 W and 25 W is shown in figure 3.1. Increasing the discharge power by 5 W increased the deposition rate by a factor of around two and is due to the sputter source removing more atoms from the tin target. In general, over time the system becomes more stable and the deposition rate improves. This makes it difficult to compare each line of data as there was a significant time between these measurements. However, it is reasonable to conclude that the rate is maximised between 80 sccm and 100 sccm. In all cases, there is a minimum
aggregation length, where the formation of clusters dramatically reduces and can no longer be measured.

3.1.2 Cluster size dependence on source conditions

The average diameter of the clusters as a function of the aggregation length and the argon flow rate for a discharge power of 20 W and 25 W is shown in figure 3.2. The average diameter of the clusters ranges between 5.5 nm and 8 nm depending on the source conditions. The size of the clusters decreases as the aggregation length is reduced and is due to the clusters having less time to aggregate. In addition, as the flow rate increases, the average diameter generally decreases. This is because an increase flow reduces the time the clusters have to aggregate.

There are two ways that the mass spectrum can change which results in a decrease in average diameter. Either the entire mass spectrum shifts (as seen in fig. 3.3a), or, the mass spectrum has a double peak and one peak reduces while the other increases (as seen in fig. 3.3b). In the latter case, the second peak corresponds to clusters that have about twice the mass as the clusters that correspond to the first peak. This indicates that there is a process where some of the clusters that would have belonged to the first peak have had time to aggregate some more to form the second peak and could correspond to circulatory flow in the source chamber.

3.2 Tin cluster film morphology

In section 1.3, we described the change in the morphology of tin cluster films produced in the UHV system when an air leak in the system was fixed. In particular, with the leak the films were granular, which produced very sensitive gas sensors previously, and without the leak the clusters in the films were highly coalesced. In this project, we looked to reproduce the film morphology when there was a leak in
Figure 3.2: The average diameter of the clusters as a function of aggregation length with a discharge power of (a) 20 W and (b) 25 W. Each line corresponds to a different flow rate of argon.

the system and to study the two different morphologies. As air consists mainly of oxygen and nitrogen, it was thought that either of these two gases was responsible for the reduced coalescence between the clusters.

This phenomenon has been observed before. Kumagai et al. [55, 56] found that the addition of either nitrogen or oxygen into the sputtering chamber of a system similar to the one used in this project resulted in reduced coalescence between the deposited tin clusters. It was concluded that the oxygen or nitrogen reacted with the surface of the clusters to form an oxide or nitride layer respectively, and that this suppressed coalescence. Olgwick et al. [57], produced copper nanoparticles using a UHV magnetron sputtering system. They found that increasing oxygen levels in the sputtering source decreased coalescence between nanoparticles and that the morphology of the individual nanoparticles changed. Turker [58] produced silver nanopowders using a high vacuum inert gas condensation system. Coalescence was also significantly reduced with the addition of oxygen into the inert gas. It was argued that the oxide layer on the nanoparticles reduced surface diffusion and sinter neck growth rate.

In this project we explored adding nitrogen into the source chamber to see the effect on the morphology of the tin films. The nitrogen we used was 99.99% pure with presumably the majority of the other 0.01% being oxygen. Therefore, the results that follow are most likely due to the nitrogen but the oxygen can not be completely ruled out. In this section, a brief introduction into island growth on substrates is given. The development of the morphology of the tin films produced when there is no nitrogen flow in the system is then studied. Finally, the effect the addition of nitrogen into the source has on the production of clusters and the morphology of the films is discussed in detail.
Figure 3.3: The mass spectrum at different aggregation lengths and with an argon flow rate of (a) 60 sccm and (b) 90 sccm. The source power is constant at 25 W. The two graphs demonstrate the two modes by which the average diameter can shift when the aggregation length is changed. In (a) the change in the average diameter of the clusters is due to the entire mass spectrum shifting. In (b) the change in the average diameter is predominately due to the shift in the height of each of the peaks.

### 3.2.1 Island growth

In many cases when atoms or clusters are deposited onto a substrate, islands form and grow in size as the deposited material increases [59]. This happens when the deposited atoms are more strongly bound to each other than to the substrate. There are three main mechanism by which islands can grow in size. Each of these mechanisms is driven by the desire of the islands to reduce their surface free energy (tension). Furthermore, they all require surface diffusion, which is the process where atoms and cluster move on a surface of a solid material.

The first mechanism is Ostwald ripening [60], this is where larger islands grow at the expense of neighbouring smaller islands, and is because smaller islands have a greater convex curvature than larger islands. This means that the surface atoms of smaller islands have less atomic bonds they can attach to and therefore have a higher probability of leaving. This leads to a net flux of atoms diffusing from smaller islands to larger islands.

The second mechanism is coalescence [61], this is where a neck grows between two islands after they make contact. Eventually the two islands form a single island. The neck growth can be explained by the convex curvature of the islands and the concave curvature of the necks. Atoms at the necks have relatively more atomic bonds than atoms on the convex surface on the islands. This leads to a net flux of atoms from the islands to the necks until equilibrium is reached. The most likely method of mass transport for sintering is surface diffusion on the islands as apposed to bulk diffusion.

The third mechanism is island migration [62], this is where the entire island
diffuses on the substrate surface and collides with a neighbouring island. It then gets absorbed by coalescence to form one larger island. This normally only occurs with an island size less than 10 nm.

3.2.2 Development of film morphology

Tin clusters were produced in the UHV compatible system and deposited on Si/SiN substrates. The thickness of the deposited films was varied to study the development of the morphology of the resulting tin films. The source conditions were set to an argon flow rate of 100 sccm, a discharge power of 25 W, and an aggregation length of 10 cm. The mass spectrum of the clusters is shown in figure 3.4 (solid curve). The deposition rate varied between 0.09 - 0.12 Å/s.

Figure 3.5 shows FE - SEM images of tin films with increasing thicknesses. These images were taken after the films had been exposed to air. At a thickness of 0.05 ML individual clusters can be seen. At thicknesses between 0.1 ML and 1 ML spherical islands begin to grow. The islands size increases as the thickness of the films increase. This behaviour can be explained by the coalescence of the clusters and islands. Clusters that are deposited in the neighbourhood of other clusters coalesce together to form islands. These islands grow as more clusters are deposited near them. At the same time, as these islands get bigger they become close enough to other islands to coalesce with them to form even bigger islands. At a thickness of 1 ML, the islands have reached a size where islands that touch do not fully coalesce and only a neck forms between the islands. This is the start of percolation and as we increase the thickness to 2 ML a percolating film develops.

This type of film growth has been well documented in literature, and is commonly observed when metals are deposited onto insulators. For instance, it has been seen when Ag has been deposited on amorphous carbon [64], and when Sn, Pb, or In has been deposited on SiO₂ [63]. Direct observation of growing metal films have shown that full coalescence occurs when metal islands are small and partial coalescence occurs when islands are above a certain size [65]. Models based on the idea, where there is a critical island size when the rate of coalescence dramatically decreases, have been shown to be in good agreement with experimental observations [63, 66].

3.2.3 The effect of nitrogen

Tin clusters were produced in the UHV compatible system and deposited on Si/SiN substrates with a flow rate of 3 sccm and 7 sccm of nitrogen into the source chamber. The thickness of the deposited films was varied to study the development of the morphology of the resulting tin films for each flow rate. The source conditions were set to an argon flow rate of 100 sccm, a discharge power of 25 W, and an aggregation length of 10 cm. The mass spectrum of the clusters for the three nitrogen flow rates is shown in figure 3.4. The deposition rate varied between 0.06 - 0.13 Å/s. In
particular, the more nitrogen that was added to the source, the more the deposition rate went down. This is due to the nitrogen poisoning the tin target. This has been observed in other sputtering systems before [67] and occurs when excess nitrogen reacts to form a nitride layer on the tin target. As the sputter yield is much less for the nitride layer, the deposition rate drops off.

Figure 3.6 shows FE-SEM images of tin films with increasing thicknesses for a nitrogen flow rate of 3 sccm. These images were taken after the films had been exposed to air. Like the films made with no nitrogen, spherical islands still grow from the deposited clusters. However, the maximum island size is much smaller, which means that there is less coalescence and surface diffusion occurring. At a thickness of 0.5 ML, islands begin to touch and partially coalesce. At a thickness of 1 ML, most islands are touching forming a granular film.

Figure 3.7 shows FE-SEM images of tin films with increasing thicknesses for a nitrogen flow rate of 7 sccm. These images were taken after the films had been exposed to air. Now, the maximum island size is around the size of the clusters themselves. The nitrogen has almost completely stopped coalescence and surface diffusion. Islands begin to touch at a thickness of 0.2 ML. There are still necks between the islands, which means they have not fully coalesced. At a thickness of 1 ML there are enough islands touching to form a granular film. This film appears very similar to the ones produced when there was a leak in the system (figure 1.1).

For a flow rate of 3 sccm, crystallites are seen growing from the film at a thickness of 1 ML. At a flow rate of 7 sccm, no crystallites can be seen. This suggests that nitrogen also reduces this growth. The crystallites also do not appear in the films produced with no nitrogen. However, in the next chapter we will see that for thicker
films of this type they play a predominate role in the films morphology.

The variation in the morphology between the films produced with and without nitrogen is most likely due to the nitrogen changing the composition of the deposited clusters. When there is no nitrogen entering the source chamber, pure tin clusters are produced. By adding nitrogen into the source, a nitride layer probably forms on the tin clusters. However this has yet to be confirmed and another possibility is that the oxygen impurities react to form an oxide layer on the tin clusters. Either way, this would affect the mobility of the clusters on the SiN substrate and the rate of coalescence. This is because the atoms in the tin nitride clusters would bond with themselves and the substrate differently for the atoms in the tin clusters.

3.3 Concluding remarks

In this chapter, we have shown that a discharge power of 25 W, an argon flow rate between 80 sccm and 100 sccm, and an aggregation length greater than 6 cm were the source conditions that resulted in the best deposition rate. The aggregation length and flow rate can be used to vary the mass distribution of the cluster and to control the average diameter of the clusters to be between 5 nm and 8 nm. In addition, we have found that the film morphology of tin cluster films deposited on Si/SiN substrates is significantly affected by the addition of nitrogen into the source. With no nitrogen, the clusters in the films were highly coalesced. With 7 sccm of nitrogen, there was very little coalescence between clusters, and the resulting films were granular.
Figure 3.5: FE-SEM images of tin cluster films produced by the UHV compatible cluster apparatus with thicknesses (a) 0.05 ML, (b) 0.1 ML, (c) 0.2 ML, (d) 0.5 ML, (e) 1 ML, and (f) 2 ML. The source conditions were set to an argon flow rate of 100 sccm, a discharge power of 25 W, and an aggregation length of 10 cm. No nitrogen was added into the system. The images were taken after the films were exposed to air.
Figure 3.6: FE - SEM images of tin cluster films produced by the UHV compatible cluster apparatus with thicknesses (a) 0.05 ML, (b) 0.1 ML, (c) 0.2 ML, (d) 0.5 ML, and (e) 1 ML. The source conditions were set to an argon flow rate of 100 sccm, a nitrogen flow rate of 3 sccm, a discharge power of 25 W, and an aggregation length of 10 cm. The images were taken after the films were exposed to air.
Figure 3.7: FE - SEM images of tin cluster films produced by the UHV compatible cluster apparatus with thicknesses (a) 0.05 ML, (b) 0.1 ML, (c) 0.2 ML, (d) 0.5 ML, and (e) 1 ML. The source conditions were set to an argon flow rate of 100 sccm, a nitrogen flow rate of 7 sccm, a discharge power of 25 W, and an aggregation length of 10 cm. The images were taken after the films were exposed to air.
Chapter 4

Tin oxide cluster film gas sensors

In this chapter, tin oxide conductimetric gas sensors made from the two distinct tin cluster film morphologies from the previous chapter are investigated. This chapter consists of four sections. The first section describes the fabrication of the gas sensors that are studied in this chapter. The second section discusses the electrical measurements made on the sensors throughout each stage of their fabrication. The third section presents the results of the hydrogen sensing experiments done with the gas sensors in the gas test rig. The final section provides a brief conclusion.

4.1 Sensor fabrication

Tin oxide gas sensors were fabricated by depositing tin cluster films onto simple samples in the UHV compatible cluster apparatus and then fully oxidising the films by baking them at 250°C for 24 hours in ambient air. Two types of gas sensors were studied. The first kind, named “Type A” sensors, were made from the films where the deposited clusters coalesced. The second kind, named “Type B” sensors, were made from the films where there was very little coalescence between the clusters. Many samples were studied, but for consistency the majority of the results in this chapter were obtained from one set of type A and type B sensors that were made on the same day, with the same conditions, and with varying thicknesses. In this section, an in depth summary of these sensors is given. A general summary for all the other sensors that were studied in this thesis can be found in table 4.1.

4.1.1 Type A sensors

Gas sensors tfw127 - tfw130, tfw132, and tfw134 were made by depositing tin clusters onto simple samples in the UHV cluster apparatus with the source conditions set to a discharge power of 25 W, an argon flow rate of 90 sccm, and an aggregation length of 11 cm. No nitrogen was added to the source. Figure 4.1 (solid curve) shows the mass spectrum, with the average cluster diameter calculated to be 7.3 nm. Table 4.2 gives a summary of the deposition rate, the onset thickness, the film thickness, and
Table 4.1: A summary of the average cluster diameter, the nitrogen flow rate into the source, the onset thickness, the film thickness, and the resistance immediately after deposition for the miscellaneous sensors that were studied in this thesis. The thicknesses were calculated from the deposition rate measured by the quartz crystal. The last column of the table gives the section where these sensors are referenced.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Average diameter (nm)</th>
<th>Nitrogen flow (sccm)</th>
<th>Onset thickness (ML)</th>
<th>Final thickness (ML)</th>
<th>Resistance (Ω)</th>
<th>Section referenced</th>
</tr>
</thead>
<tbody>
<tr>
<td>tfw68</td>
<td>8.2</td>
<td>5</td>
<td>0.66</td>
<td>1.0</td>
<td>326</td>
<td>2.5.3</td>
</tr>
<tr>
<td>tfw69</td>
<td>8.2</td>
<td>5</td>
<td>0.66</td>
<td>1.5</td>
<td>200</td>
<td>2.5.3</td>
</tr>
<tr>
<td>tfw83</td>
<td>7.0</td>
<td>10</td>
<td>0.51</td>
<td>2.0</td>
<td>280</td>
<td>4.2.2</td>
</tr>
<tr>
<td>tfw137</td>
<td>7.0</td>
<td>7</td>
<td>0.54</td>
<td>1.0</td>
<td>1670</td>
<td>4.2.2</td>
</tr>
</tbody>
</table>

The resistance immediately after deposition of these sensors. The thicknesses were calculated from the deposition rate measured by the quartz crystal.

The morphology of these sensors was surveyed by taking FE-SEM images of tfw129, tfw127, and tfw134. These sensors were chosen as their thicknesses span the thicknesses of all the sensors. Figure 4.3 shows FE-SEM images of these sensors between the electrodes and at one of the electrodes. For the 2 ML sensor, tfw129, the morphology is similar to the films deposited on plain Si/SiN in the previous chapter (see figure 3.5). However, now the film has reached percolation and is nearly continuous. For the 4 ML and 6 ML sensors, tfw127 and tfw134, the first monolayer of growth has finished and there is now a second monolayer of growth on the films.

On each film, there are also crystallites that have formed, which increase in size with film thickness. These have been seen before on many other sensors of this type that have been made during this project. The reason for their growth is unknown. The crystallites seem to increase in number closer to the electrodes, which suggest the electrodes are having an effect on their growth. Figure 4.2 shows an example of the electrode boundary of a clean simple sample. Instead of having a well defined edge, the thickness of the deposited gold decreases over some distance on the substrate and is due to the use of the shadow mask. This may be the cause for the distribution of crystals seen in figure 4.3. It could be possible that the gold particles are increasing the rate of coalescence within their neighbourhood, which assists the crystallite growth.

4.1.2 Type B sensors

Gas sensors tfw93 - tfw99 were made by depositing tin clusters onto simple samples in the UHV cluster apparatus with the source conditions set to a discharge power
Figure 4.1: Mass spectrum of the tin clusters used to produce the type A sensors tfw127-134 (solid curve) and type B sensors tfw93-99 (dotted curve).

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Deposition rate (Å/s)</th>
<th>Onset thickness (ML)</th>
<th>Final thickness (ML)</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tfw127</td>
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<td>4.4</td>
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</tr>
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<td>tfw129</td>
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<td>42</td>
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<tr>
<td>tfw134</td>
<td>0.06</td>
<td>2.0</td>
<td>6.0</td>
<td>37</td>
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Table 4.2: A summary of the deposition rate, the onset thickness, the film thickness, and the resistance immediately after deposition for the type A sensors tfw127-tfw134.

of 25 W, an argon flow rate of 80 sccm, a nitrogen flow rate of 7 sccm, and an aggregation length of 11 cm. Figure 4.1 (dotted curve) shows the mass spectrum with the average cluster diameter calculated to be 7.0 nm. Table 4.3 gives a summary of the deposition rate, the onset thickness, the film thickness, and the resistance immediately after deposition of these sensors.

The morphology of these sensors was surveyed by taking FE-SEM images of tfw97, tfw95, and tfw93. These sensors were chosen as their thicknesses span the thicknesses of all the sensors. Figure 4.4 shows FE-SEM images of these sensors between the electrodes and at one of the electrodes. For the 1 ML sensor, tfw97, the morphology is similar to the films deposited on plain Si/SiN in the previous chapter (see figure 3.7). For the 2 ML and 4 ML sensors, tfw95 and tfw93, the morphology is the same, only the thickness has increased. The gold electrodes seem to have very little effect on the film morphology. However, for the sensors tfw97 and tfw95, there is a narrow dark strip at the electrode edge in the FE-SEM images, which may indicate that this area is a nonconducting gap.
<table>
<thead>
<tr>
<th>Sensor</th>
<th>Deposition rate (Å/s)</th>
<th>Onset thickness (ML)</th>
<th>Final thickness (ML)</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
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<td>243</td>
</tr>
<tr>
<td>tfw94</td>
<td>0.065</td>
<td>0.72</td>
<td>4.2</td>
<td>281</td>
</tr>
<tr>
<td>tfw95</td>
<td>0.060</td>
<td>0.75</td>
<td>2.2</td>
<td>620</td>
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</table>

Table 4.3: A summary of the deposition rate, the onset thickness, the film thickness, and the resistance immediately after deposition for the type B sensors tfw93-tfw99.

Figure 4.2: FE-SEM image of an electrode from a simple sample with no deposited film.
Figure 4.3: FE-SEM images of the film morphology between the simple sample electrodes (left column) and at one of the electrodes (right column) for tfw129, tfw127, and tfw133, which have a thickness of (a) 2 ML, (b) 4 ML, and (c) 6 ML respectively.
Figure 4.4: FE-SEM images of the film morphology between simple sample electrodes (left column) and at one of the electrodes (right column) for tfw97, tfw95, and tfw93, which have a thickness of (a) 1 ML, (b) 2 ML, and (c) 4 ML respectively.
4.2 Electrical measurements

Over the course of deposition, venting, and baking, the resistance of the gas sensors changes considerably. This is due to the morphological and compositional changes happening in the tin cluster films. In this section, the conductivity of the sensors at each of these stages is discussed. In particular, the conductivity of the coalesced films is compared against the uncoalesced films, and where possible the films produced when there was a leak in the system.

4.2.1 In situ

The conductivity of each sensor was measured throughout their deposition. This was done to find out if and when the sensors became conductive and how their conductivity developed as their thickness increased. This can be used to gain some insight on how the morphology of the films develops. Figure 4.5 shows the current through the sensors tfw93 and tfw128 as their thicknesses increase during their deposition. A constant voltage of 50 mV was applied across the gold electrodes. These curves show the common features that were seen during the deposition of the type A and B sensors.

To begin with, the current through the sensors is virtually zero. After a certain thickness of material has been deposited, the current increases dramatically. This is the time of onset and is when the film has reached percolation and begins to conduct. The onset thickness for a type A sensor is generally greater than that for a type B sensor. From the data in table 4.2 and table 4.3 we can calculate the average onset thickness for the type A and B sensors to be 1.7 ML and 0.7 ML respectively. This is consistent with the films deposited on clean Si/SiN substrates in the previous chapter where we saw percolating coalesced and uncoalesced films at 2 ML and 1 ML respectively.
Figure 4.6: *The resistance of the type A sensor, tfw128, and the type B sensor, tfw93, after onset as a function of film thickness.*

Figure 4.6 shows the resistance of tfw93 and tfw128 during deposition after the initial onset of current has occurred. The resistance of tfw128 very quickly reaches a constant value at around 70 Ω. On the other hand, the resistance of tfw93 continues to slowly decreases until the end of deposition, where its final resistance is 243 Ω. This is much higher than that for the type A sensor. There are two reasons for this. The composition of the deposited clusters are different. The coalesced film has been made with pure tin clusters whereas the uncoalesced film has been made with tin clusters with either a nitride or oxide layer. Furthermore, the uncoalesced film has more grain boundaries, which has the effect of decreasing conductivity due to grain boundary scattering of electrons.

Figure 4.7 (diamond points) show the resistances of the type A sensors tfw127-134 and the type B sensors tfw93-99 immediately after deposition. The data points correlate well with what is seen in figure 4.6, which shows that the sensors are reasonably consistent with each other. When there was a leak in the system, the resistance of a typical film was measured to be in the order of a MΩ [48]. This is at least three orders of magnitude greater than when the films are produced with either no leak or with the addition of nitrogen to the source. Retrospectively, the high resistance of the films when there was a leak indicated that the films were most probably oxidised in some way. It also means that there is a significant difference between the films produced with the addition of nitrogen into the source and with the leak. This is mostly likely due to a difference in the compositions of the clusters that are deposited in the two cases. Either, the clusters produced with nitrogen are less oxidised than those produced with the leak, or they have a nitride layer instead of an oxide layer. This difference in compositions may have an effect on coalescence between clusters as well, and this could also influence the resistance of the films.
Figure 4.7: The resistance of the (a) type B sensors, tfw93-99, and the (b) type A sensors, tfw127-134, when they were in situ, after they were baked, and when they were at 200°C in dry air.

4.2.2 Venting

Figure 4.8 shows the resistance of two type B sensors, tfw83 and tfw137, during and after the deposition chamber had been vented. These sensors have a thickness of 1 ML and 2 ML respectively. The resistance was measured by applying a constant voltage of 50 mV across the sensors. For both sensors, the resistance increases over time until they were practically nonconductive and is due to the surface of the films being oxidised when exposed to air. The porous nature of the films means that much of the film gets oxidised, which results in a significant decrease in conductivity. The 1 ML film oxidises much faster than the 2 ML film as it has a larger surface to volume ratio.

Figure 4.9 shows the resistance of the type A sensor, tfw134, during and after the deposition chamber had been vented. The resistance was measured by applying a constant voltage of 50 mV across the sensor. In this case, there is very little change in the sensors resistance. This is because the sensors film has very large grains due to the coalescence of clusters, and when air oxidises the surface there is still a metallic bottom layer on the film that is highly conductive.

4.2.3 After baking

Figure 4.7 (circle points) shows the resistance of the type A and B sensors, tfw127-134 and tfw93-99, after they were baked for 24 hours at 250°C. The resistance was found by applying a voltage of 0.5 V across the sensors and then measuring the current. Each of the sensors’ resistance is much higher compared to when they were produced in UHV as the sensor films are now tin oxide (SnO$_2$). For the type B sensors, the general trend that resistance decreases with increasing thickness still applies after baking. For the type A sensors, we also see a similar trend, but we note here that this was not present when the sensor films were metallic. In general,
the resistance of the coalesced sensors is less than the uncoalesced sensors with the same thickness. This is most likely due to the large number of grain boundaries in the uncoalesced films resulting in more grain boundary scattering of the electrons.

Figure 4.7 (triangle points) shows the resistance of type A and B sensors, tfw127-134 and tfw93-99, when they are at 200°C in dry air. In all cases the resistance increases. This is because the films are semiconductors, which means more thermal energy results in more electrons being excited to the conduction band. For the type A sensors, the resistance increases by a factor of two. For the type B sensors the increase in resistance is different for each sensor.

4.3 Hydrogen tests

In this section, we report on the experiments we did with the sensors in the gas test rig. In particular, we discuss the effect that the film morphology, the film thickness, and the temperature of the sensors have on their response to hydrogen.
4.3.1 Hydrogen response

The response of the sensors tfw93-99 and tfw127-134 to 500 ppm, 1000 ppm, and 5000 ppm of hydrogen in dry air was tested in the gas test rig. The resistance of the sensors was measured by applying a constant voltage of 0.5 V across them and then measuring the resulting current. The temperature of the sensors was set to 200°C to increase absorption and desorption rates to get a reasonable response from the sensors. At the same time, we did not want to set the temperature higher than the baking temperature of 250°C as we wanted to avoid any further changes to the morphology of the sensor films.

Figure 4.10 shows the cycle that each sensor went through. For the first hour, no gas ran through the system. This was done to find the resistance of the sensors after baking. For the next 9 hours, 100 sccm of dry air flowed into the chamber. During this time, the temperature was increased from room temperature to 200°C, and the resistance of the sample was allowed to reach equilibrium. From then on, the response of the sensors to different concentrations of hydrogen was tested in 6 hour cycles. This provided enough time for the resistance of each sensor to be close to equilibrium during and after their exposure to hydrogen.

An example of the resistance of a sensor during this run is shown for tfw96 in figure 4.11. The resistance of the sample decreases when exposed to hydrogen, which is expected for a tin oxide film. This is due to the hydrogen reducing the ionosorbed oxygen in the tin oxide. This increases the charge carriers and hence increases the conductivity of the sensor. The response increases with the hydrogen concentration as more hydrogen results in more desorption of oxygen in the tin oxide films.

To compare each gas sensor, we need a measure for their response. In this thesis, we define the response as \((R_f - R_i)/(R_i)\), where \(R_i\) and \(R_f\) are the resistances before and after the sensors are exposed to hydrogen. Figure 4.12 shows the response of the
Figure 4.11: The resistance of the sensor tfw96 during a run where it has been exposed to 500 ppm, 1000 ppm, and 5000 ppm of hydrogen.

sensors tfw93-99 and tfw127-134 to 500 ppm, 1000 ppm, and 5000 ppm of hydrogen in dry air as a function of their film thickness. The responses of the type B sensors are significantly better than the type A sensors. This is due to the two different film morphologies. The type B sensor films have more surface area and smaller grain boundaries which results in better gas sensing properties. For the uncoalesced films, there is a significant increase in the sensitivity of the sensors when the film thickness is 1 ML. The most likely explanation for this is that these films have a higher surface to volume ratio than the thicker films, which results in better sensitivity.

4.3.2 Temperature dependance

The response of sensors tfw95 and tfw129 to 5000 ppm of hydrogen was measured for temperatures ranging from 50°C to 400°C in the gas test rig. This was done to find how their performance changes with temperature. These particular sensors were chosen as examples of the type A and B sensors. Both sensors are 2 ML thick and showed a good response to hydrogen in the previous section. The measurements were made in the following way. A voltage of 0.5 V was used to measure the resistance of the sensors except for tfw95 at the temperatures 50°C and 100°C where a voltage of 2.5 V was needed to get a measurable current. At each temperature, we waited until the resistance of the sensors reached equilibrium and then exposed them to 5000 ppm of hydrogen for three hours and then again waited until their resistance reached equilibrium.

Figure 4.13 shows the resistance of the two sensors as a function of temperature. In both cases, their resistance decreases nonlinearly with temperature, which is consistent with the films being semiconductors. For all temperatures, the resistance of the coalesced sensor is two orders of magnitude less than the uncoalesced sensor.

Figure 4.14 shows the response of the two sensors when exposed to 5000 ppm of hydrogen gas as a function of temperature. For all temperatures, the type B sensor
Figure 4.12: The response as a function of film thickness for the type A (closed circles) and type B (open triangles) sensors at 200°C for hydrogen concentrations (a) 500 ppm, (b) 1000 ppm, and (c) 5000 ppm. The data corresponds to the sensors tfw93-99 and tfw127-134.

remains more sensitive than the type A sensor. The response of tfw95 increases quickly from 100°C to 200°C and continues to slowly increase thereafter. On the other hand, the response of tfw129 steadily increases up until 300°C and decreases at 400°C.

Figure 4.15 and 4.16 show the resistance of tfw95 and tfw129 during exposure to 5000 ppm of hydrogen at different temperatures respectively. In both cases, at 100°C the response time is very long and the sensor does not recover back to its initial resistance. The response time is significantly reduced as the temperature increases due to increased absorption and desorption rates. For tfw95, at 300°C it appears that there may be some instability in the resistance in the film as it is exposed to hydrogen. After a large initial decrease, the resistance of the sensor begins to increase. This may be a sign of morphological changes occurring. A similar behaviour occurs for tfw129 at 400°C.

The optimal operating temperature for tfw95 appears to be around 200°C as the sensitivity barely changes with further increases in temperature. The optimal operating temperature appears to be a bit higher at around 300°C for tfw129.
Figure 4.13: The resistance of the type A sensor, tfw129, and the type B sensor, tfw95, at temperatures between 50°C and 400°C.

Figure 4.14: The response of the type A sensor, tfw129, and the type B sensor, tfw95, to 5000 ppm of hydrogen at temperatures between 50°C and 400°C.

4.3.3 tfw99

The sensor tfw99 was shown to be one of the most sensitive gas sensors in section 4.3.1. For this reason, we tested the sensors response to a larger range of hydrogen concentrations. Figure 4.17 shows the resistance of the sensor as it is exposed to between 200 ppm and 5000 ppm of hydrogen at 200°C. A voltage of 2.5 V was used to measure the resistance of the sensor. The sensor was exposed to each concentration of hydrogen for three hours and given another three hours to return to its original resistance. The sensor shows a definite response to a hydrogen concentration as low as 200 ppm. Figure 4.18 shows that the response increases linearly with the log of the concentration of hydrogen.
Figure 4.15: The resistance of the type B sensor tfw95 as it is exposed to 5000 ppm of hydrogen for 3 hours at a temperature of (a) 100°C, (b) 200°C, (c) 300°C, and (d) 400°C.

4.4 Concluding remarks

In this chapter, we have shown that the tin oxide gas sensors made from the uncoalesced films are significantly more sensitive to hydrogen than those made from the coalesced films. This is attributed to the higher surface to volume ratio and the small grain size of the uncoalesced films. As mentioned in chapter 3, the uncoalesced films have a similar morphology to the gas sensors made previously by Lassesson et al when there was an air leak in the UHV system. However, those sensors showed over an order of magnitude change in resistance when exposed to 5000 ppm of hydrogen at 80°C. This could either be due to the different contact geometries used in that study or because there was even less coalescence between the deposited clusters in those films making them more granular and therefore more sensitive. From the electrical measurements made in section 4.2, we know that the differences begin when the films are first deposited. It is likely that when there was a leak, the clusters became far more oxidised compared to when we added nitrogen into the source. In future experiments, it would be interesting to see how adding pure oxygen into the source affects the film morphology and if this can be used to make more sensitive sensors.
Figure 4.16: The resistance of the type A sensor tfw129 as it is exposed to 5000 ppm of hydrogen for 3 hours at a temperature of (a) 100°C, (b) 200°C, (c) 300°C, and (d) 400°C.

Figure 4.17: The resistance of the sensor tfw99 as it is exposed from 200 ppm to 5000 ppm of hydrogen in 6 hour cycles at a temperature of 200°C.

Figure 4.18: The response of the sensor tfw99 to hydrogen concentration between 200 ppm to 5000 ppm at a temperature of 200°C.
Chapter 5

Conclusion

In this thesis, tin clusters formed in the UHV compatible cluster apparatus by DC magnetron sputtering and inert gas aggregation was studied. It was found that when the tin clusters are deposited onto silicon nitride substrates, they coalesce, and form films that are very similar to those that are seen in atomic deposition of metals onto insulators. This is contrary to what was found previously, where tin cluster were used to produce films with very little coalesce and with grain sizes close to that of the deposited clusters.

The difference between these two results was put down to there being an air leak in the system, which was fixed when this thesis was started. We assume that when there was a leak, the oxygen in the air reacted with the tin clusters before they were deposited onto the substrate. This formed a tin oxide layer on the clusters, which significantly reduced their mobility on the substrate and the coalescence between them. In this thesis, we showed that we could replicate this effect by adding nitrogen into the source of the cluster system. However, we are not sure whether it was the nitrogen that reacted with the clusters or the trace amounts of oxygen in the nitrogen. Furthermore, we found that a lot of nitrogen was needed to reduce coalescence. This caused the problem of sputter target poisoning, which significantly reduced the deposition rate. Future work would be to see the effect of adding oxygen into the source as this might fix this problem as it reacts quickly with tin.

Lassesson et al. [47] showed that tin oxide films produced by tin clusters when there was a leak in the system made very good gas sensors. This was because the film had a very large surface to volume ratio and a small grain size due to the very little coalescence between the deposited clusters. In this thesis, we made similar gas sensors from the films produced with no leak and with the addition of nitrogen in the source. The latter sensors, due to the reduction in coalescence between clusters, showed a much better responses to hydrogen than the former sensors. However, neither showed the same response as the sensors produced by Lasseson et al. It was concluded that this was due either to the contact geometry of the sensors or because the films produced with nitrogen was still more coalesced then the films produced with the leak. Future work would be to explore the contact geometry and
use oxygen instead of nitrogen to try to further reduce coalescence.

Another question that is still to be completely answered is whether baking the tin cluster assembled films at 250°C for 24 hours completely oxides them to SnO₂. Many experiments have indicated this to be true. We hope to get a definitive answer to this question with the use of powder diffraction in the near future.

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