2002

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GROWTH DEPENDANT PROPERTIES OF UNDOPED AND IN-SITU DOPED CHEMICALLY DEPOSITED CdS THIN FILMS

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Honours Thesis

Faculty of Communications, Health and Science

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Perth Western Australia

Bachelor of Science Honours (Physical Science)

June 2002

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USE OF THESIS

The Use of Thesis statement is not included in this version of the thesis.

ABSTRACT

This research project examines the growth dependant properties and composition of Cadmium Sulfide thin films produced by the Chemical Bath Deposition Method. The specific areas investigated are the effect of deposition temperature, the effect of an Indium dopant on the films structure and properties, and the effects of post deposition processing such as annealing in air on the film composition.

The chemical bath deposition apparatus used has been refined and tested to ensure that the films were grown in a more efficient manner than previously, with more control of the influencing deposition parameters such as temperature. Films grown by the CBD method with this apparatus were durable, yellowish in colour, and adherent to the glass substrates used. The CdS thin films were then subjected to a number of analysis techniques to determine their properties. These techniques include Proton Induced X-ray Emission, Atomic Force Microscopy, Secondary Ion Mass Spectroscopy, Environmental Scanning Electron Microscopy with Charge Contrast Imaging, and Photoconductivity.

The results from the analysis of the CdS thin films revealed the presence of nodule structures on the surface of the annealed films. Films produced at lower deposition temperatures seemed to have increased sulfur deficiencies, resulting in an increased Cadmium to sulfur ratio. The Indium doping was found to be inhomogeneous through the depth of the film. The Indium doping concentration in the deposition was also found to be consistent with the concentration found in the films by analysis. Higher deposition temperatures were found to encourage the deposition of colloidal particulates on the surface of the substrates. Annealing of the CdS was found to produce films with surface features that were rougher in appearance.

Declaration

I certify that this thesis does not, to the best of my knowledge and belief:

(I)   incorporate without acknowledgement any material previously submitted for a

degree or diploma in any institution;

(II)   contain any material previously published or written by another person except

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Date 25/10/2002

Acknowledgements

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INTRODUCTION

The primary purpose of this project is to examine the growth dependant properties of Cadmium Sulfide (CdS) deposited by the Chemical Bath Deposition (CBD) method in the form of a thin film. Through this undertaking, it is hoped to gain an understanding of the defect structure, the effect of in-situ doping and post deposition processing on these Cadmium Sulfide thin films.

1-1 Properties of CdS

CdS is a II-VI semiconductor, meaning its constituents come from the second and sixth periods of the periodic table. CdS as a semiconductor has a large band gap between its valance band and conduction band, approximately 2.4 eV. This means that at room temperature it is almost an insulator. Thin film CdS is an intrinsic slightly n-type semiconductor, due to a sulfur deficiency in the films (Mahanty et al., 1999). Typically, CdS is doped with elements such a Indium to promote it's n-type semiconducting nature. This has the effect of decreasing the band gap and providing more charge carriers for the conduction of current. CdS appears as a yellowish coloured crystalline substance, and for the purpose of this project is in the form of a thin film deposited on a slide. This unique substance also has the added benefit of being transparent and very durable.

1-2 Chemical Bath Deposition

The technique used to deposit the CdS on a substrate in this study will be the Chemical Bath Deposition method. This process is cheap, simple and operates at a relatively low temperature between 60 and 80°C. Several processing effects will be examined to gain a greater understanding of how they impact on the optoelectronic properties. These processes include in-situ doping and post-deposition annealing. Doping concentration will be examined as will the effect of annealing at a temperature of 400°C.

1-3 Research Questions

CdS is a very versatile substance in that its properties can be tailored to some degree by altering the conditions under which it is produced. To understand how these production conditions influence the properties of CdS a few questions need to be answered.

Firstly, what is the effect of in-situ doping on the CdS thin films? When considering the effects of in-situ doping the specific properties being examined are surface morphology and the optoelectronic properties.

What are the effects of in-situ doping on the morphology and defect structure of the films surface?

What are the effects of in-situ doping on the optoelectronic properties of the CdS thin films, specifically the dark conductivity and the photosensitivity?

Also, does the in-situ doping incorporate the Indium into the lattice structure of the CdS?

What is the effect of changing the temperature at which the CdS thin films are deposited onto the substrates?

What is the effect of post deposition processing on the CdS thin films? This can be further broken down.

What is the effect of annealing the CdS thin films at high temperatures as opposed to leaving them as-deposited?

Finally what effect does the atmosphere have on the CdS thin films during the annealing process?

1-4 Objectives

The main objective of this study is to gain a greater understanding into the properties of CdS thin films that are influenced by the aspects of its growth and post deposition processing. This objective is achieved by defining a number of aims:

Design and refine the CBD apparatus used to grow the CdS thin films for the purpose of increasing efficiency and stability of the CBD system.

Grow a range of CdS thin films with varying Indium dopant levels at a range of different deposition temperatures.

To anneal a full set of the created films and compare their properties with the as-deposited films.

To conduct a series of optoelectrical measurements to determine photosensitivity and dark conductivity of the CdS films, and the effects Indium doping and annealing may have.

Analyse as-deposited and annealed CdS films with a range of surface analysis techniques such as SIMS, ESEM, CCI, and PIXE, and gain an understanding of these analysis tools, along with the type of information they can give.

1-5 Limitations

Several limiting factors were encountered while conducting this study.

The SIMS and PIXE analysis conducted on the CdS thin films made possible by a grant supplied by AINSE for work at ANSTO was to be completed within 5 days. Time on both the SIMS and PIXE was extremely limited and there was no availability for extra time, which meant that only a small number of samples could be examined. Unfortunately, during the time that the PIXE measurements were to be conducted the 3MV accelerator was unavailable due to extensive technical difficulties and maintenance issues. The samples that were to be analysed with PIXE had to be left behind and analysed by staff at the ANSTO facility at a later date. This placed considerable restrictions on the ability to gain any experience using the PIXE

equipment. Only a qualitative analysis of the SIMS samples could be conducted as no standard sample of CdS was available for quantitative Analysis.

1-6 Safety

Due to the dangerous nature of the chemicals being handled and Edith Cowan University's policy on Occupational Safety and Health, several steps were taken to ensure safety while experimenting with CdS and its related chemicals.

Firstly, Material Safety Data Sheets (MSDS) were obtained for all the relevant chemicals, so that possible risks that exist in dealing with these substances could be identified. A copy of the relevant MSDS can be found in Appendix A. The following measures were taken in accordance with the information obtained from the MSDS.

All experimentation with chemicals was conducted in a fume cupboard. Personal protective equipment was worn, including a laboratory coat, safety goggles, and latex gloves. All glassware equipment was cleaned after each use. When produced, all samples were stored in resealable plastic containers and handled with gloves and tweezers.

REVIEW OF THE LITERATURE

2-1 Uses and applications

CdS has a multitude of uses and applications in several important areas of study. This is due to an increasing interest that has been received by CdS as a wide energy band gap semiconductor. As a result a range of applications has been developed such as terrestrial photovoltaic solar cells, piezoelectric transducers, imaging displays, and material used in the construction of lasers (Vazquez-Luna, 1998).

Heterojunction solar cells that consist of numerous types of narrow band gap semiconductors such as $CuInSe_2$, $CuInS_2$, InP, Cu2S require a window layer. Here CdS's use as a direct band gap II-VI semiconductor is being exploited. By controlling the composition of the CdS thin film, the band gap can be influenced in order to be more responsive to different solar spectra that are absorbed in the window layer (Mahanty et al., 1999). CdS thin films of are also being found suitable for applications in imaging and visual displays in the form of Thin Film Transistors (TFT). Here thin films of CdS can be used to produce circuits on large area, low temperature substrates (Gan & Shi, 2002). CdS has also been found useful in such applications as photoconductive detectors (e.g. Light Dependant Resistors), and as a possible passivation layer in HgCdTe photodetectors.

2-2 Properties needed for applications

There is currently a wide variety of applications that CdS films can be utilised in. This is attributed to the far reaching properties of the films, and the ability to tailor the properties of the CdS by manipulating the production conditions.

CdS has been recently recognised as a good candidate in the active layer of Thin Film Transistors (TFT) used in electronic displays and imaging applications (Gan & Shih, 2002). For CdS to be useful in this area a number of specific properties are required. The CdS TFT will require a relatively large on/off current ratio. The hall mobility μ_H and field effect mobility μ_{FE} have to be in the region of that of amorphous Silicon. When the TFT is in the off state, the leakage current between the drain and source

should be quite small, less than 10pA. Also the current in the on state at a given voltage should be relatively large, greater than 1μA. The TFT's threshold voltage (V_T) must be small ($V_T = 2.5V$), and a large mobility is required of the charge carriers in the channel ($\mu_{FE} = 0.2\text{-}1.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

For a number of years now CdS has been considered and is being developed as a window layer in solar cells for terrestrial use. Typically the solar cell is constructed as a heterojunction composed of CdTe, CdS, and a transparent conducting oxide (TCO). In this type of junction, the CdTe is used as the solar cell absorber layer. The TCO provides a highly transparent (>90%) conductive coating making electrical contact to the CdS. For the CdS layer to be useful in this area, it must satisfy several requirements. Firstly, the CdS film should be conductive, and it should have charge carriers in the vicinity of n~ 10^{16} cm^{-3}. This is to ensure that the cell resistance is kept to a minimum. Secondly, the CdS film should be quite thin to allow for a high transmission of light through to the CdTe layer, as charge carriers generated in the CdS layer are generally lost. However, the primary concern for the CdS layer is that it prevents surface recombination loss in the CdTe layer. Typically acceptable values for film thickness are between 50 and 100 nm. Lastly, the films have to be uniform over the cell; if this requirement is not satisfied short circuit effects will occur (Durose et al., 1999).

CdS thin films are also well suited in applications such as photodetectors and other photoconductive devices. There are two key properties that a good photodetector should possess. The first is a low dark conductivity. When the detector is in the absence of any light, the device should have a relatively low conductivity. The other property the device should have is a good photosensitivity. When the photodetector is in the presence of light, the resistance of the device should change dramatically. The ideal photoconductor has a large difference in conductivity between the off state when there is no light and the on state when there is light.

2-3 CBD growth and deposition

There are many methods available for producing CdS thin films. Some of these include Molecular Beam Epitaxy, Thermal Evaporation, Sputtering, Chemical Vapor Deposition, Electrodposition, Spay Pyrolysis and Chemical Bath Deposition (Mahanty

et al., 1999). Of these processes, the CBD method is the simplest and relatively cheapest method available, as the equipment required is readily available in most chemistry laboratories and the chemicals used are quite inexpensive. The method is particularly suited to large scale depositions, as it can form consistent films that are smooth, hard, and pinhole free. Additionally, this method can produce near stoichiometric CdS due to growth kinetics inherent in the method (Al Kuhaimi & Tulbah, 2000).

The CBD of CdS revolves around the combination of cadmium and sulfide ions in solution. There are three major chemicals involved in this reaction. Thiourea $CS(NH_4)_2$ provides the sulfide ions for the deposition process. Cadmium Acetate $Cd(CH_3COO)_2$ provides the Cadmium ions to be deposited, and Ammonia NH_3 affects the pH of the CBD system and effectively controls the ion by ion deposition rate. The complete reaction of the CBD system is:

$$Cd(NH_3)_4^{+2} + CS(NH_2)_2 + 2OH^- \Rightarrow CdS + CH_2N_2 + NH_3 + 2H_2O \quad [2\text{-}3\text{-}1]$$
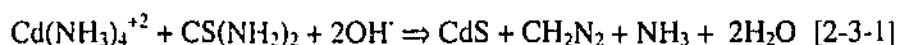
This formula gives a general idea of reagents used and products produced. However, it does not show how each reagent interacts with the system in the chemical bath. To examine the purpose of each reagent Equation 2-3-1 needs to be broken up. Equation 2-3-2 shows the formation of Cadmium Hydroxide from Cadmium ions and Hydroxide ions present from dissolved Cadmium and Ammonia, respectively.

$$Cd^{+2} + 2OH^- \Leftrightarrow Cd(OH)_2 \quad\quad\quad [2\text{-}3\text{-}2]$$

Sulfide ions are formed through the hydrolysis of Thiourea and hydroxide ions:

$$CS(NH_2)_2 + 2OH^- \Rightarrow S^{-2} + CH_2N_2 + 2H_2O \quad\quad\quad [2\text{-}3\text{-}3]$$
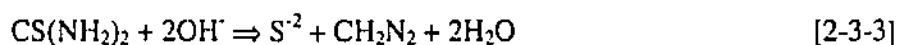
The controlled release of Cadmium ions can then be facilitated by the decomplexing of Cadmium:

$$Cd(NH_3)_4^{+2} \Leftrightarrow Cd^{+2} + 4NH_3 \quad\quad\quad [2\text{-}3\text{-}4]$$

Cadmium Hydroxide then participates is an exchange of Sulfide ions for Hydroxide ions:

$$Cd(OH)_2 + S^{-2} \Leftrightarrow CdS + 2OH^- \qquad [2\text{-}3\text{-}5]$$

The Cadmium and Sulfide ions then combine to form CdS:

$$Cd^{+2} + S^{-2} \Rightarrow CdS \qquad [2\text{-}3\text{-}6]$$

The Ammonia dissolves in the CBD system and complexes with the free Cadmium ions as follows:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \qquad [2\text{-}3\text{-}7]$$

$$Cd^{+2} + nNH_3 \Leftrightarrow Cd(NH_3)_n^{+2} \qquad [2\text{-}3\text{-}8]$$

$$Cd(OH)_2 + 4(NH_3) \Leftrightarrow Cd(NH_3)_4^{+2} + 2OH^- \qquad [2\text{-}3\text{-}9]$$
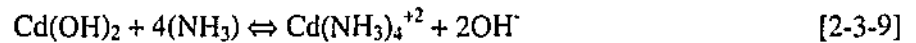
While the solubility product remains dominate in regards to the ionic product of CdS, an ion by ion deposition system will be the predominant deposition process. When the solubility product is exceeded by the ionic product, the formation of particulates in the solution and on the substrates will be predominant (Gluszak, 1996). Figure 2-3-10 shows a graph of the pH of the system vs Cadmium ion concentration. Two lines are shown, the hydroxide and complex lines for Cadmium. The shaded area in region I between the hydroxide line and the complex line, along with the shaded area just above the hydroxide line in region II, show conditions which are optimal for producing thin films via the ion by ion deposition system (Duncan, 2001). With this model the deposition conditions can be controlled to produce a chemical reaction inside the shaded regions.
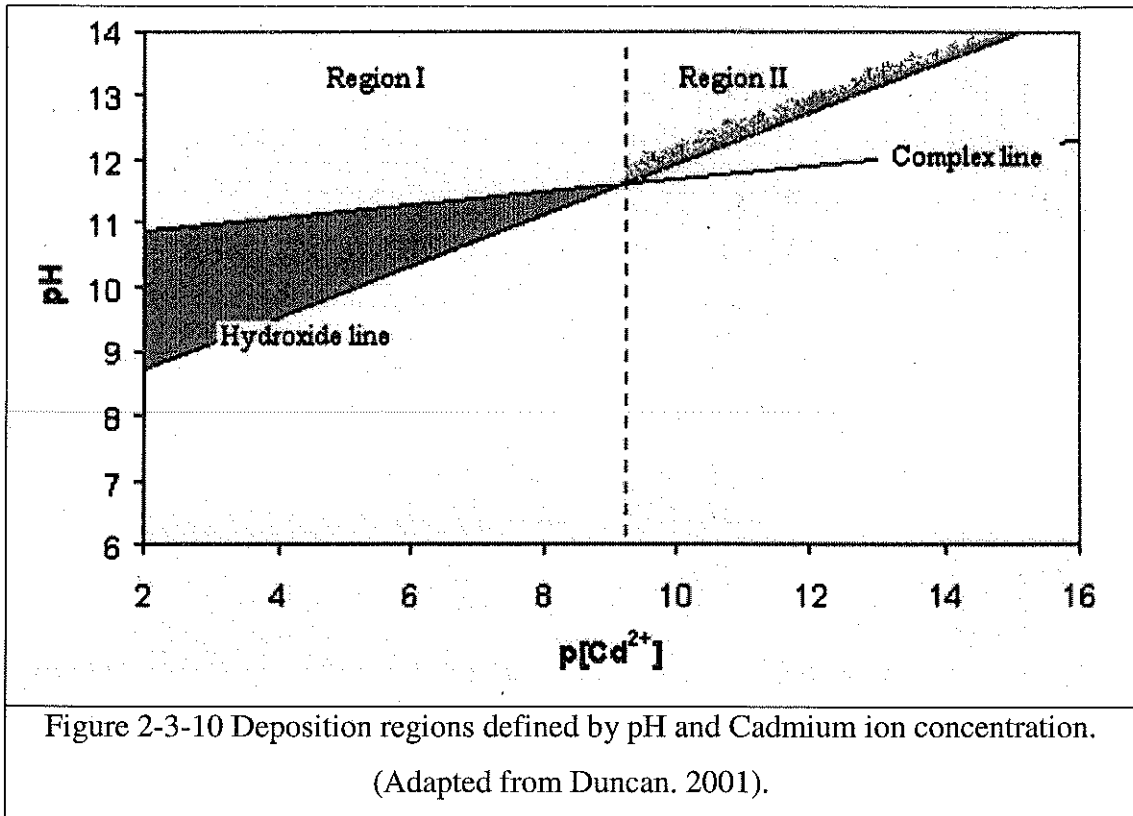
Figure 2-3-10 Deposition regions defined by pH and Cadmium ion concentration.
(Adapted from Duncan. 2001).

2-4 As-deposited CBD CdS Properties

Various production aspects such as deposition conditions, doping, and post deposition processing influence the properties of CdS films. The deposition of the films is one of the more significant aspects, as it affects the composition of the CdS films directly. The temperature used in depositing the films, the concentration of the reagents, the length of time used to deposit the CdS, and the pH of the CBD system all contribute to the result of the deposition.

There exists a large quantity of information concerning CdS films produced by the CBD method. A firm grounding in the optoelectrical properties of these films does not yet exist, as evidenced by the disagreement of data reported by different authorities. This can be accounted for when one considers the relationship between the optoelectrical properties, the film microstructure and how the post deposition processing and deposition conditions interact. For example, the dopant level, film microstructure and film thickness act directly to vary the films electrical resistivity by several orders of magnitude. The temperature the films are deposited at, and the composition of the chemical bath solution, can influence the optical absorption coefficient. The energy

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band gap can be reduced via annealing in different gases (Rakhshani & Al-Azab, 2000). Where appropriate quantities of reactants are available, films can be made to exhibit increased on-currents and field effect mobilities by depositing them at raised temperatures and pH values (Gan & Shih, 2002). By increasing the Cadmium to Sulfur, ratio the band gap (E_g) can be decreased, this relationship being very close to linear. When the film is near stoichiometric the band gap is in the region of 2.43 eV (Mahanty et al., 1999). Figure 2-4-1 shows the relationship between Cadmium-Sulfur ratio and the band gap.
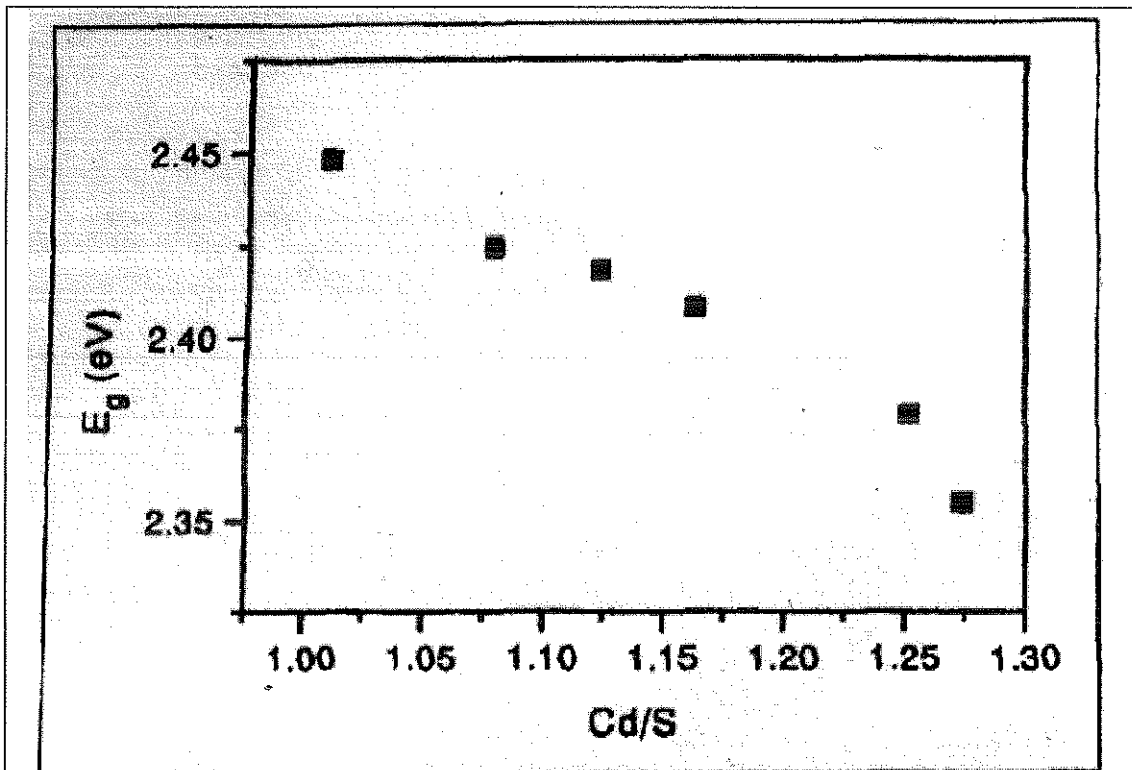

Figure 2-4-1 Relationship between Cd/S ratio and the energy band gap (Adapted from Mahanty et al., 1999).

Table 2-4-2 gives a brief summary of the studies done by other researchers on the CBD method and their main points.

Table 2-4-2 Summary of previous studies.

Deposition Type	Study Description	Comments	Reference
CdS CBD	Growth modes of Solution grown CdS thin films.	Formation of CdS films in CBD is brought about by two growth modes, ion by ion condensation and colloidal particles of CdS adhering to substrate surfaces. Bath composition affects the film growth modes.	Sebastian et al., 1995
ZnCdS CBD	ZnCdS films for solar cell and photodetector applications deposited by in situ chemical doping of CdS with Zn.	Photosensitivity of CdS increases with doping and increases with increasing concentration of dopant. Dark conductivity of doped CdS films improves with annealing.	Sebastian, 1995
CdS CBD	Cadmium sulfide thin films prepared by chemical bath deposition method.	The deposition rate of films is increased by conditions of higher temperature and/or higher pH values. There is a weak increasing tendency in the film thickness with the increase of the pH value	Kuranouchi et al., 1994
CdTe/CdS junction CdS CBD	Materials aspects of CdTe/CdS solar cells.	Studies show a 10-20% excess of Cd over S which can be attributed to the presence of $Cd(OH)_2$ and CdO. Heating in air eliminates water from $Cd(OH)_2$ to give CdO.	Durose et al., 1999
CdS CBD	Optical and electrical characterization of CdS films.	CdS films annealed in $CdCl_2$ flux for 10 minutes at 400°C exhibit a much larger grain size than as-deposited films.	Ozan et al., 1996
CdS CBD	Microstructural effects of thermal annealing on CdS films.	One effect of thermal annealing on CdS films deposited by CBD is the occurrence of a band gap shift. Thermally treated samples show an optical gap lower than the band gap.	Galvan et al., 1996

Electrical measurements carried out at room temperature on as-deposited CdS films indicate that they are highly resistive, greater than 10^6 s. Composition measurements using Energy Dispersive Analysis of X-rays (EDAX), indicate that the as-deposited

films have a Cadmium to Sulfur ratio greater than one and are therefore deficient in Sulfur (Mahanty et al., 1999).

2-5 Effect of Doping

Doping is another important aspect in the production of CdS, particularly in areas where electrical conductivity is concerned. The type of dopant used and its concentration in the CdS film has a significant effect on the electrical properties. When considering dopant quantities, the molar concentration of the dopant should be below that of Cadmium and Sulfur in the deposition system.

When semiconductors such as CdS are doped with other materials such as Indium, the optical characteristics change due to the formation of impurity energy levels within the band gap. One of these impurity energy levels corresponds to a donor level approximately 0.1eV below the conduction band, due to sulfur vacancies. Cadmium vacancies will produce an acceptor level 1.1eV above the valence band. Indium will also produce an acceptor level above the valence band due to Indium vacancies (Sebastian, 1995).

Photosensitivity of CdS will increase when doped with an impurity such as Indium. Increasing the concentration of the dopant will have the effect of increasing the photosensitivity further still. This is due to the increase in vacancies present with the dopant, the dopant vacancies together with the Cadmium and Sulfur vacancies produce photosensitisation centers in the CdS thin film (Sebastian, 1995).

2-6 Post deposition processing

Post deposition processing covers the annealing of the CdS films at different temperatures anywhere between 150 and 400°C and has a marked impact on the structural and electrical properties. Specifically, the crystallinity and electron mobility can be manipulated. The duration of the annealing process and the type of gas atmosphere or vacuum used are also important components of the annealing process.

As-deposited CdS films have been found to have relatively low electron mobilities. By annealing them the quality of the crystal structure can be improved, which increases the

mobility of electrons (Gan & Shih, 2002). Stoichiometric CdS films that are annealed in air have an excess of Cadmium present, whereas the same film annealed in a vacuum has been found to be in excess of Sulfur (Mahanty et al., 1999). Annealing in an air atmosphere also has the effect of increasing the donor density very slightly above that of the as-deposited CdS thin films. Annealing in a $CdCl_2$ atmosphere has the effect of increasing the donor density level by approximately three times (Ozan et al., 1996).

Annealing decreases the band gap energy markedly. This is due to the conversion of some of the CdS to other compounds. Annealing in air introduces Oxygen and water vapour into the system, which will be absorbed and then diffuse into the film's lattice interacting with the other components (Gluszak & Hinckley. 1999).

The effect of the annealing temperature on the films is very important as it will determine the potential usefulness of the substance. One of the properties affected by annealing is the photosenitivity defined as:

$$S = (I_{ph} - I_{dark}) / I_{dark} \qquad\qquad [2\text{-}6\text{-}1]$$

Where I_{ph} is the current in the semiconductor where illumination is present, and I_{dark} is the current in the dark. Unannealed films are highly resistive in the dark, with a dark resistance of $0.25 \times 10^3 \Omega$-cm, and a photosensitivity of approximately 10^3 (Gluszak & Hinckley). CdS thin films annealed up to a temperature of 150°C have a markedly increased photosensitivity of 10^6. Annealing the CdS thin films at 200°C decreases the photosensitivity to approximately 10^4, and annealing at temperatures above this further decreases the photosensitivity, however, this is due to an increase in the dark current by approximately 10^4. Annealing at temperatures up to 400°C will lead to a large decrease in the Sulfur. The loss of the Sulfur takes place through the reaction. (Gluszak & Hinckley.1999):

$$2CdS + 3O_2 \Rightarrow 2CdO + 2SO_2 \qquad\qquad [2\text{-}6\text{-}2]$$
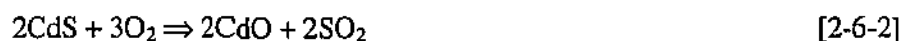
Due to the loss of Sulfur, additional vacancies are created which work to improve the dark conductivity. The increased dark carrier concentration in the CdS thin film leads to a decreased photosensitivity according to equation 2-6-2. (Sebastian, P. J. 1995).

THEORY

There is a large quantity of literature concerning the theory of semiconductors. In this section, priority is given to the material directly relating to the optoelectronic, structural properties and composition being examined. These include the band theory of solids, photoconductivity, atomic force microscopy, proton induced x-ray emission, secondary ion mass spectroscopy, and charge contrast imaging.

3-1 Band Theory of Solids

The band theory of solids explains the process by which charge carriers are generated, move through a solid, the electron conduction process, and optical properties. All solids are grouped together into three main categories, conductors, insulators and semiconductors. The operation of conductors and insulators is fairly elementary and not really relevant. However, semiconductors behave in a more interesting manner and have a direct relationship to the optoelectronic properties being examined.

When atoms are brought close together, their wave functions overlap, splitting the possible energy levels that are available. When there are a large number of atoms brought together such as in a solid, the energy levels split into almost continuous bands. This is illustrated in Figure 3-1-1.
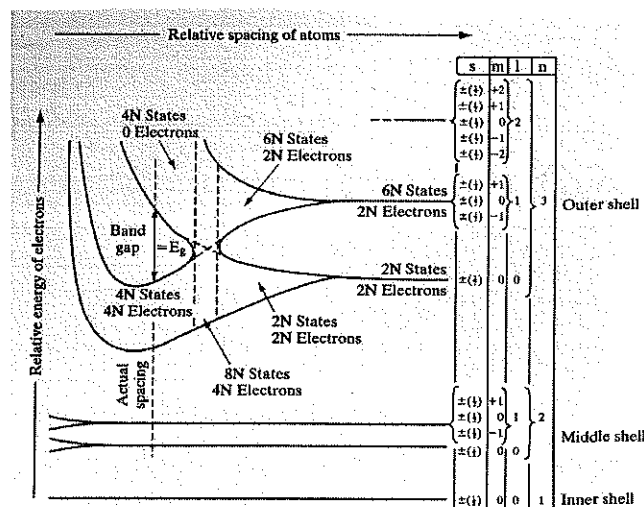

Figure 3-1-1 Splitting of energy levels to form energy bands (adapted from Streetman & Banerjee, 2000).

Band theory describes a semiconductor as having two bands, a valence band and a conduction band separated by a band gap. The valence band is defined as the highest occupied band at absolute zero, and contains the valence electrons. The conduction band is the next band up, higher in energy and is generally empty at absolute zero. These two bands are separated by the energy band gap, which is a forbidden zone where electron states due to the host lattice do not exist. This is shown in Figure 3-1-2.
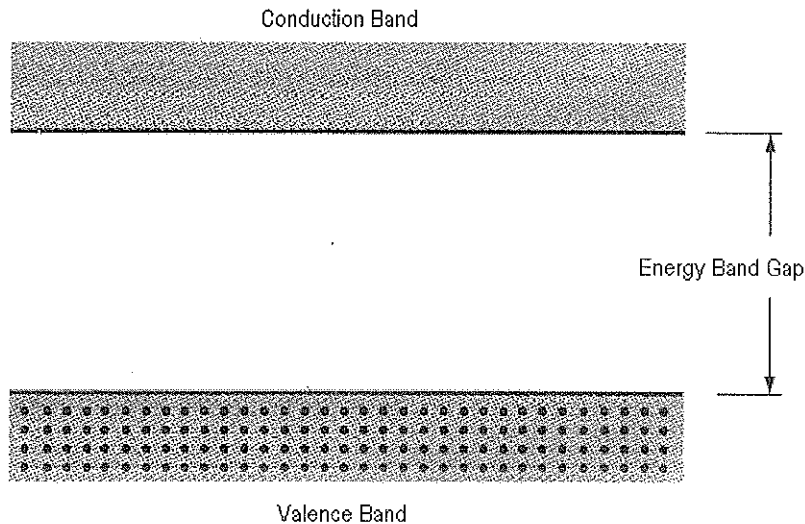
Figure 3-1-2 Energy level diagram of a semiconductor (adapted from Streetman & Banerjee, 2000).

In its lowest energy state, a semiconductor has no available charge carriers, meaning the valance band is filled and the conduction band is empty. This means the semiconductor can conduct no current hence, at absolute zero, all semiconductors are insulators. However, when electrons become excited by an appropriate amount of energy, they can jump the band gap from the valence band to the conduction band thus generating an electron hole pair. The band gap or forbidden energy band is shown in Figure 3-1-2 as E_g. Holes can be considered a vacant electron state in the valence band that move in the opposite direction to electrons. Electron energy increases upwards through the valence and conduction bands, whereas hole energy increases downwards through the conduction and valence bands. Electrons and holes in a crystal lattice can not be considered to be completely free, as they interact with the periodic potential of the lattice. This can be accounted for by changing the actual mass of the charge carrier to an effective mass as shown by:

$$m_n^* = (h/2\pi)^2/(d^2E/dk^2)$$
$$[3-1-3]$$

Where m_n^* is the effective mass of an electron (kg), h is Planck's constant (J-s), E is the energy (J), and k is the wave vector (cm^{-1}).

A semiconductor is said to be intrinsic when its lattice structure is perfect. Extrinsic semiconductors on the other hand are created when doped to change the intrinsic equilibrium carrier concentration of electrons and holes. Doping is used to create charge carriers in a semiconductor by introducing impurities into the crystal lattice. It is used to vary the conductivity of the semiconductor. Doping alters a semiconductor so that it has a predominance of electrons or holes. This produces two types of semiconductors, n-type that have mostly electrons as charge carriers, and p-type that have mostly holes as charge carriers. When impurities or defects are introduced into the crystal structure, energy levels are created in the band structure, usually within the forbidden gap. This is shown in Figure 3-1-4.

Figure 3-1-4 Diagram showing the donor and acceptor energy levels in a semiconductor (adapted from Streetman & Banerjee, 2000).
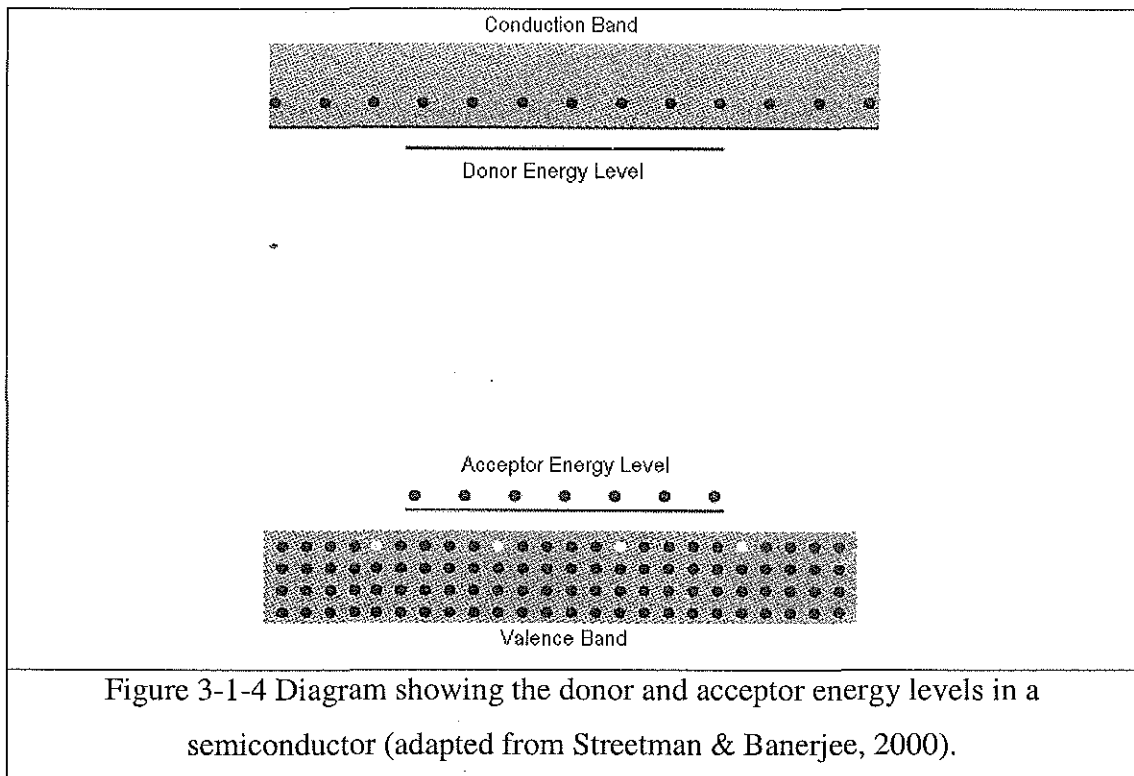
Energy levels that are created near the conduction band donate electrons to the conduction band, and these levels are thus referred to as donor levels. At absolute zero,

these donor levels are full of electrons. Very little energy is generally required to promote electrons from the donor level to the conduction band, which increases the materials conductivity at lower temperatures. This produces semiconductors with large numbers of electrons in the conduction band and are generally referred to as n-type semiconductors. Impurity energy levels created near the valence band accept electrons from the valence band, and for this reason are called acceptor impurity levels. At absolute zero, these energy levels are devoid of electrons, and very little energy is required to excite electrons from the valence band to this impurity level, thus also increasing the conductivity of the semiconductor at lower temperatures by creating holes in the valence band. Doping of this type creates materials with much greater hole concentrations in the valence band than electrons in the conduction band, and are termed p-type semiconductors. The electron and hole concentrations can be represented by:

$$n_0 = n_i e^{(E_i - E_f)/kT} \qquad [3\text{-}1\text{-}5]$$

$$p_0 = n_i e^{(E_f - E_i)/kT} \qquad [3\text{-}1\text{-}6]$$

Where n_i is the intrinsic electron concentration (cm^{-3}), E_i is the intrinsic Fermi level (J, eV), E_f is the equilibrium Fermi level (J, eV), k is Boltzmann's constant (J/K, eV/K), and T is the temperature (K). It should be noted that n_i is the carrier concentration due only to the temperature of the semiconductor, in the absence of doping and impurities. This electron-hole pair generation process also occurs in the reverse direction and is called carrier recombination. In recombination, the electron loses energy and falls back down to the valance band, combining with a hole. In between these two processes the two charge carriers are free to conduct current across the semiconductor. The recombination of electron hole pairs can proceed in two ways, direct and indirect recombination, shown in Figure 3-1-7.

Figure 3-1-7 Direct and Indirect recombination in a semiconductor (adapted from Streetman & Banerjee, 2000).
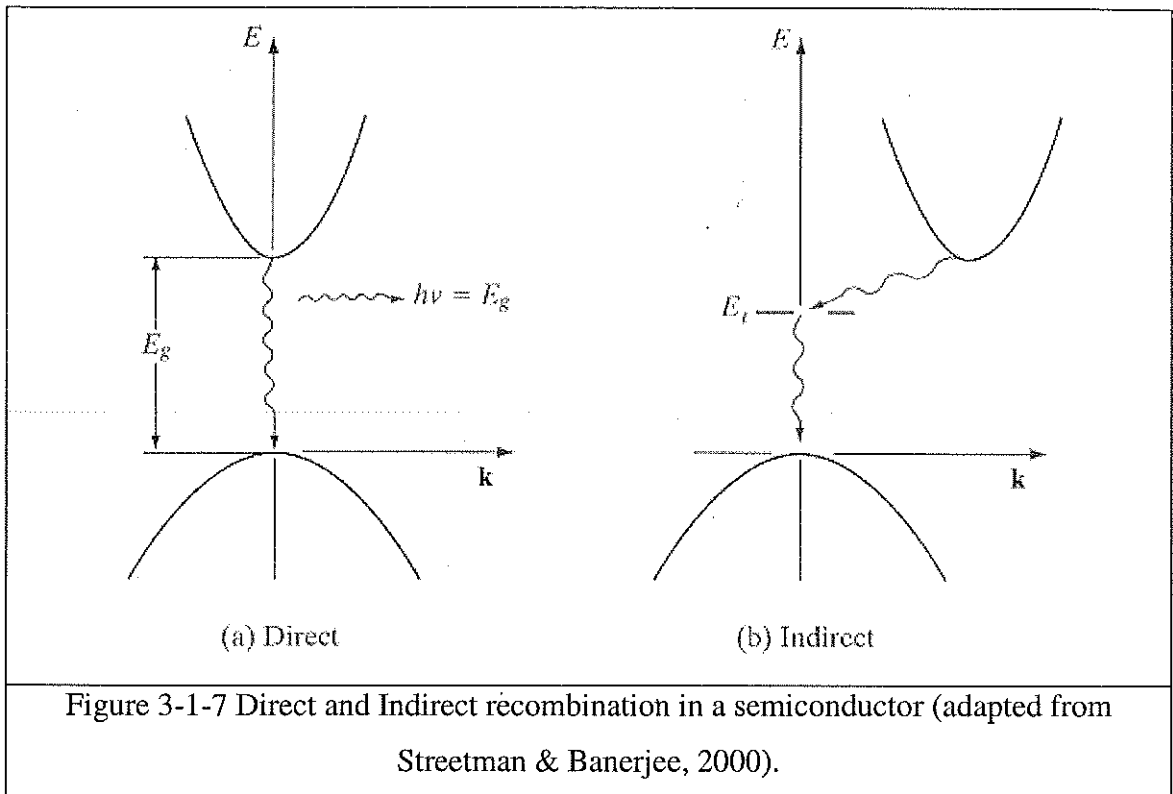
In direct recombination, the electron-hole pairs decay by electrons moving from the conduction band down to the valence band and annihilating with a hole, the energy lost is given up as a photon. The time between when charge carriers are generated and recombine is termed the carrier lifetime, and in direct recombination is given by:

$$\tau_n = 1/\alpha_r(n_0 + p_0) \qquad\qquad [3\text{-}1\text{-}8]$$

Where τ_n is the recombination lifetime of electrons(s), α_r is the recombination coefficient (cm^3/s), n_0 is the equilibrium electron concentration (cm^{-3}), and p_0 is the equilibrium hole concentration (cm^{-3}).

Indirect recombination occurs via recombination impurity levels or traps present within the energy band gap. The energy lost through these recombinations is less than that given up in direct recombination, and is passed to the lattice as heat. Recombination levels are the result of impurities and lattice defects, that are able to capture both types of charge carriers thus annihilating an electron hole pair. The carrier lifetime for indirect recombination is far more complex than that for direct recombination. The recombination time is dependant on the time for two opposite charges to be captured. If the recombination site does not capture the second charge carrier immediately after the

first, then it may be thermally re-excited. This means the first charge carrier must then be recaptured. Recombination by way of trap levels deeper in the energy band gap take longer as more energy is required than levels closer to the band edges. The distribution of electrons in the many energy levels as a function of E and T is determined by the Fermi-Dirac distribution:

$$F_{FD} = 1/(B_1 \exp(E/(kT)) + 1)$$ [3-1-9]

Where B_1 is a normalisation constant, E is the energy (J,eV), k is Boltzmann's constant (J/K, eV/K), and T is the temperature in Kelvin. At absolute zero all the atoms in the solid are in the ground state. When the temperature is increased, more atoms are expected to be in excited states and thus the probability of finding an electron that has jumped the energy gap into the conduction band is higher. Therefore, the higher the temperature, the more electrons are expected to be promoted from the valence band to the conduction band. This causes the resistance of the semiconductor to decrease. The general relationship is that resistance in semiconductors decreases exponentially with increasing temperature (Thornton & Rex, 1993).

3-2 Photoconductivity

Photoconductivity is very similar to the photoelectric effect in that photonic radiation energises electrons making them more mobile. This increases the number of charge carriers and has a direct effect on the resistivity or conductivity of the semiconductor material. For a uniform semiconductor, the resistance in Ω is:

$$R = \rho L/wt = L/wt\sigma$$ [3-2-1]

Where L is the length (cm), w is the width (cm), t is the thickness (cm), ρ is the resistivity (Ω-cm), and σ is the conductivity $(\Omega\text{-cm})^{-1}$.
The conductivity can be shown as:

$$\sigma = qn\mu_n + qp\mu_p$$ [3-2-2]

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Where q is the charge of an electron (C), n and p are the concentrations of electrons and holes, respectively, μ_n and μ_p are the electron and hole mobilities (cm^2/V-s), respectively. The electron and hole mobility is described as:

$$\mu_n \equiv qt/m_n^* \qquad\qquad [3\text{-}2\text{-}3]$$

$$\mu_p \equiv qt/m_p^* \qquad\qquad [3\text{-}2\text{-}4]$$

Where t is the mean free time between scattering collisions (s), and m_n^* and m_p^* are the effective masses of an electron and a hole (kg), respectively.

When light impinges on the semiconductor, electron-hole pairs are generated which change the material conductivity. Figure 3-2-5 shows the excitation (a), lattice scattering (b) and recombination (c) of an electron in a semiconductor band structure.
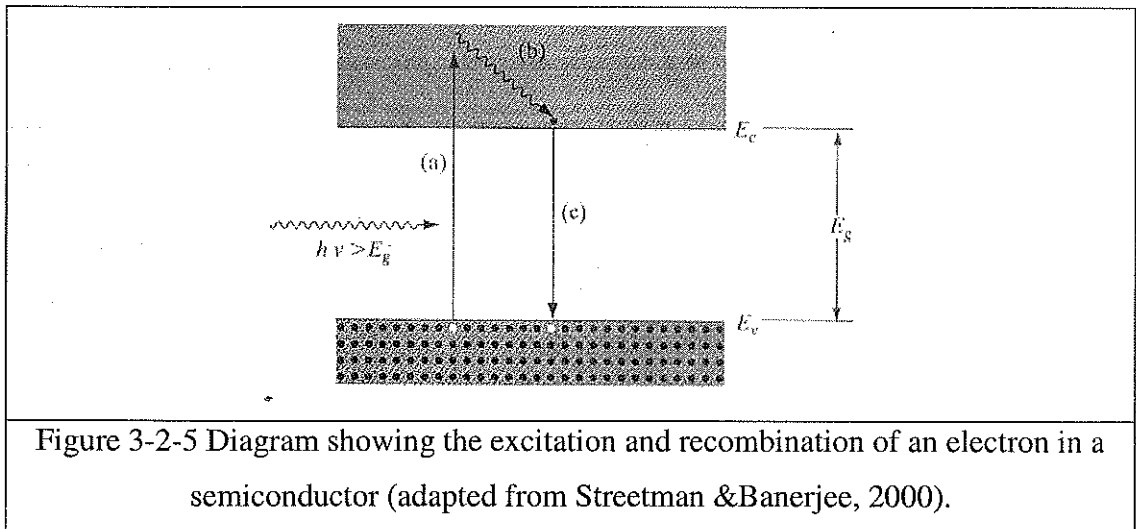
Figure 3-2-5 Diagram showing the excitation and recombination of an electron in a semiconductor (adapted from Streetman &Banerjee, 2000).

When an external electric field ξ_x is applied to the semiconductor in the x direction, the electrons experience a net force of $-q\xi_x$. If p_x is the x component of the total momentum of n electrons, the force of the electric field on n electrons is:

$$-nq\xi_x = dp_x/dt \qquad\qquad [3\text{-}2\text{-}6]$$

The electrons and holes then move in opposite directions, leading to a flow of current (Singh, 1994). The current in the x direction due to the flow of electrons and holes is:

$$J_x = q(n\mu_n + p\mu_p)\xi_x = \sigma\xi_x \qquad\qquad [3\text{-}2\text{-}7]$$

A bias potential applied along the length of the semiconductor provides the electric field that will separate the electron-hole pairs. Light then needs to impinge on the semiconductor's surface. This light must be of an energy high enough to excite the electron to a state where it has sufficient energy to move to the conduction band. The increase in charge carriers in the conduction band reduces the resistance so that a larger current can flow in an external circuit. The change of conductivity due to impinging light where both holes and electrons are present is be given by:

$$\Delta\sigma = q\delta_p\mu_p + q\delta_n\mu_n \qquad\qquad [3\text{-}2\text{-}8]$$

Where q is the magnitude of the electronic charge (C), δ_p and δ_n are the excess hole and electron concentrations (cm^{-3}), μ_n and μ_p are the electron and hole mobilities ($cm^2/V\text{-}s$). When considering semiconductors in such technology as solar cell applications, measuring the photoconductivity can be a very useful tool. Many important characteristics can be determined about the semiconductor, including conductivity which is directly related to carrier recombination life time under different intensities of illumination, and the effect of doping on the e-h pair generation under illumination. This type of information could go a long way in helping to determine the best dopant levels to use (Streetman &Banerjee, 2000).

3-3 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is used to perform surface imaging with atomic resolution. The atomic force microscope works by measuring the force between the surface of the sample and the scanning tip of the microscope. This force is typically very small, usually less than 10^{-9} Newtons. The forces in question are not measured directly by the microscope. Instead, the deflection of a microcantelever attached to the scanning tip is measured which gives an indication of the force. There are two main atomic force microscope classifications or modes of operation, repulsive (contact mode) and attractive (non-contact mode).

3-3-1 Operation

The operation of the microscope is fairly simple, the schematic diagram of an AFM is shown in Figure 3-5-1. An atomically sharp tip, usually composed of Si_3N_4 or Si, is scanned over the surface of the sample. The microscope has a feedback system that makes it possible for scanners to keep the tip at a constant height. This provides force information about the surface. The detection system on the atomic force microscope has relatively few moving parts. First a reflective cantilever can be positioned over the sample. The scanning tip is attached to the underside of this cantilever. A laser beam is then focused onto the top reflective side of the cantilever. The reflected beam is redirected via a mirror to a dual element photodiode, which measures the difference in light intensities and converts it to a signal voltage. Data collected from this information enables three dimensional topographical maps to be constructed showing the surface detail. There are three modes of operation, contact mode, non-contact mode, and tapping mode which can be considered intermittent contact.
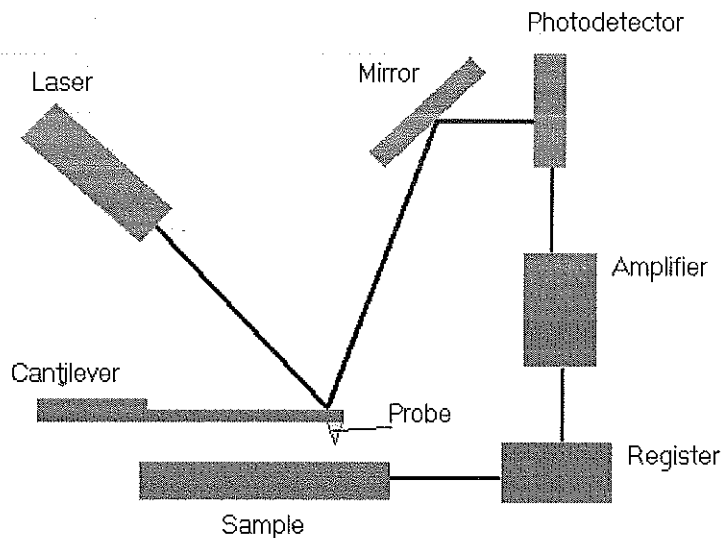
Figure 3-5-1 Schematic diagram of an Atomic Force Microscope (adapted from Hong-Giang. 1997).

3-3-2 Contact Mode

In contact mode, the tip is used to scan the surface in close contact. Figure 3-5-2 shows the position of the probing tip with respect to the sample's surface. This is the most common mode of operation. The force produced on the tip is a repulsive force with a mean value usually around 10^{-9} Newtons. In this mode, a piezoelectric positioning element is used to set the force. It does this by pushing the cantilever against the

surface. The deflection of the cantilever can then be measured and a comparison can be made in a feedback amplifier. When there is a difference in deflection the feedback amplifier can be used in conjunction with the piezoelectric positioning element to provide small height adjustments to the sample relative to the cantilever, which will act to maintain a constant deflection value.
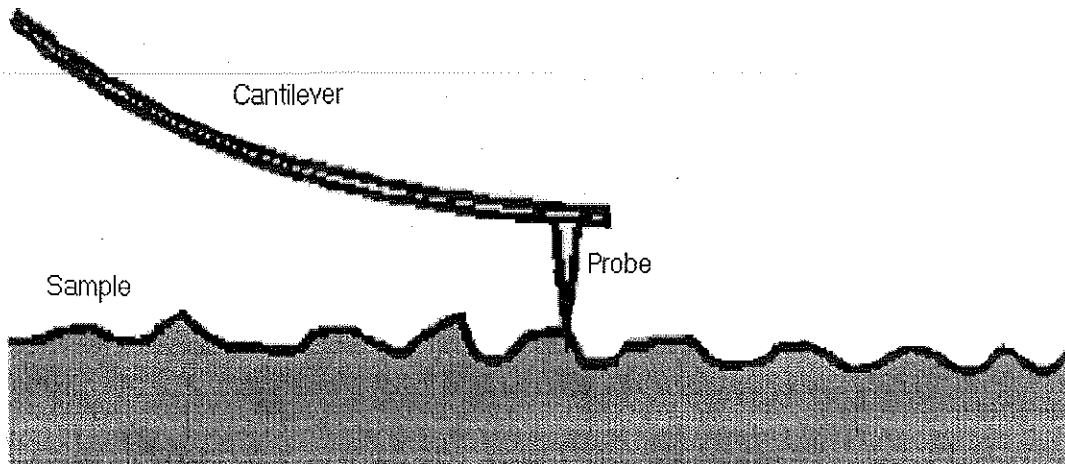
Figure 3-5-2 Position of cantilever and probe in contact mode (adapted from Hong-Qiang 1997).

3-3-3 Non-Contact Mode

The non-contact mode is used when contact of the tip with the sample can cause problems. The tip is placed about 50 to 150 angstroms above the sample surface, as shown in Figure 3-5-3. In this mode of operation, the forces being measured are the attractive Van der Waals forces acting between the sample and the tip. The forces present in this mode are markedly weaker than those present in contact mode. The other main difference between this mode and contact mode is that AC detection methods are used so the tip has to oscillate. The data collected from this mode of operation can be used to construct topographical information about the sample's surface.
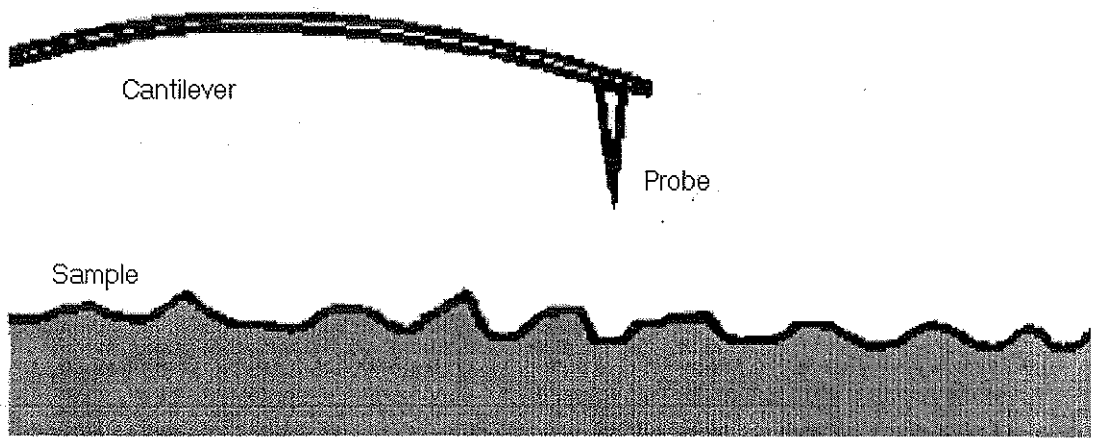
Figure 3-5-3 Position of cantilever and probe in non-contact mode (adapted from Hong-Qiang, 1997).

3-3-4 Tapping Mode

Tapping mode is used when problems such as friction, adhesion, and electrostatic forces need to be avoided. Using a piezoelectric crystal, the cantilever oscillates near its resonant frequency with an amplitude usually greater than 20 nm. The oscillation frequency is between 50kHz and 500kHz. The oscillation of the cantilever is kept constant by means of a feedback loop. When the cantilever comes in close proximity with the surface, the amplitude of the oscillation is reduced. This reduction in amplitude is measured and used to determine the aspects of surface features (Hong-Qiang, 1997). Figure 3-5-4 shows the oscillation of the probe with respect to the surface of the sample.
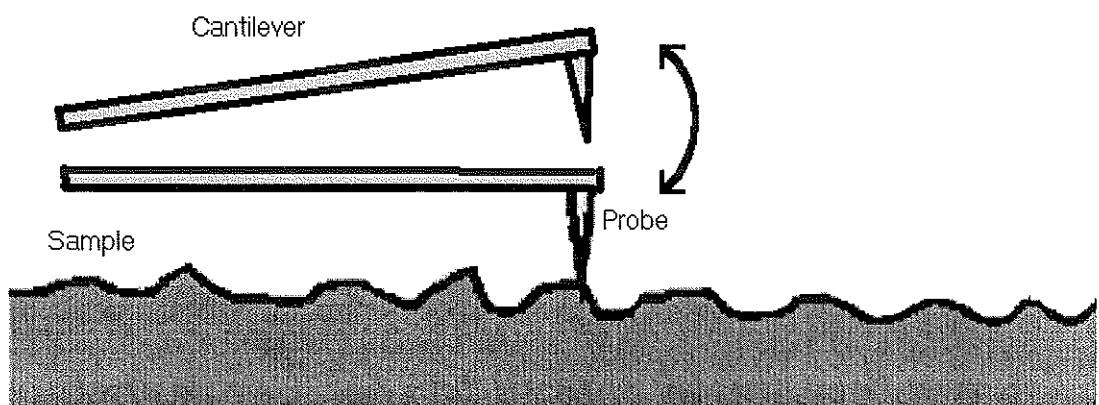

Figure 3-5-4 Position of cantilever and probe in tapping mode adapted from Hong-Qiang, 1997).

Regardless of the mode used to gather data, the AFM simply provides topographical information of the surface detail present. Most AFMs come with analysis software that can use this information to determine information such as grain size and surface roughness.

3-4 Proton Induced X-ray Emission

Proton Induced X-ray Emission (PIXE) is an excellent non-destructive analytical technique for quantifying and identifying elements in trace amounts. The technique is suitable for detection of the elements ranging from Aluminium to Uranium. The sensitivity of the instruments used typically ranges from 1-100 ppm. It is also important to note that PIXE only probes 10 to 50μm into the surface of the sample.

The technique involves targeting a beam of protons at the surface of the sample being examined. The protons lose energy to electrons as they move through the sample material. Excited electrons, particularly the K and L shell electrons, gain enough energy to be ejected resulting in an unstable electronic configuration. Electrons in higher shells fall down to replace the lost electrons and in doing so give off energy in the form of X-rays. This process is shown in Figure 3-6-1. Also, Figure 3-6-2 shows the typical arrangement of an accelerator and detectors used for PIXE.

Each element in the periodic table emits X-rays characterised by specific energies. By examining the spectrum of X-ray energies given off, one can determine the different elements present and their concentrations. A list of elements and their characteristic X-rays has been placed in Appendix D. PIXE is a bulk analysis process where a comparatively large area of the sample is observed as a whole. This can be compared to SIMS where the analysis is conducted on a relatively small area of the sample and is taken relative to depth.
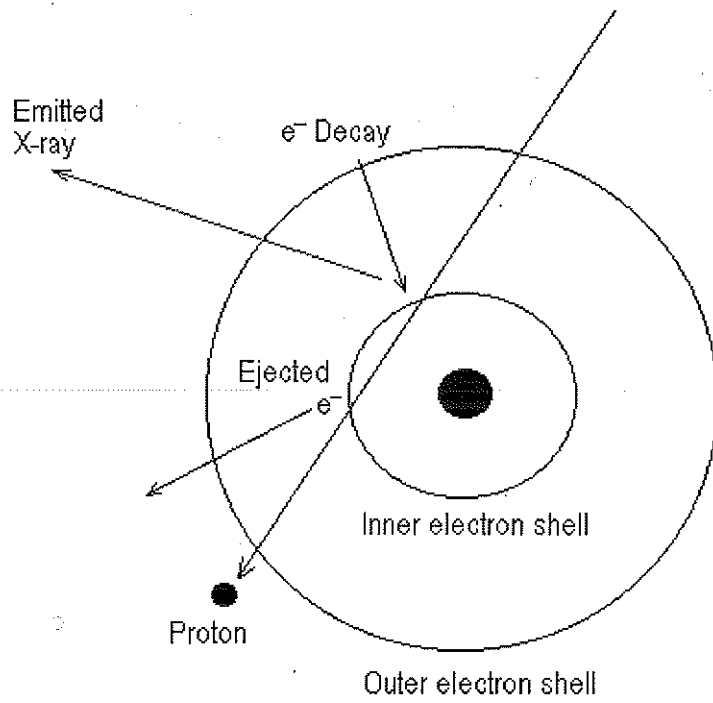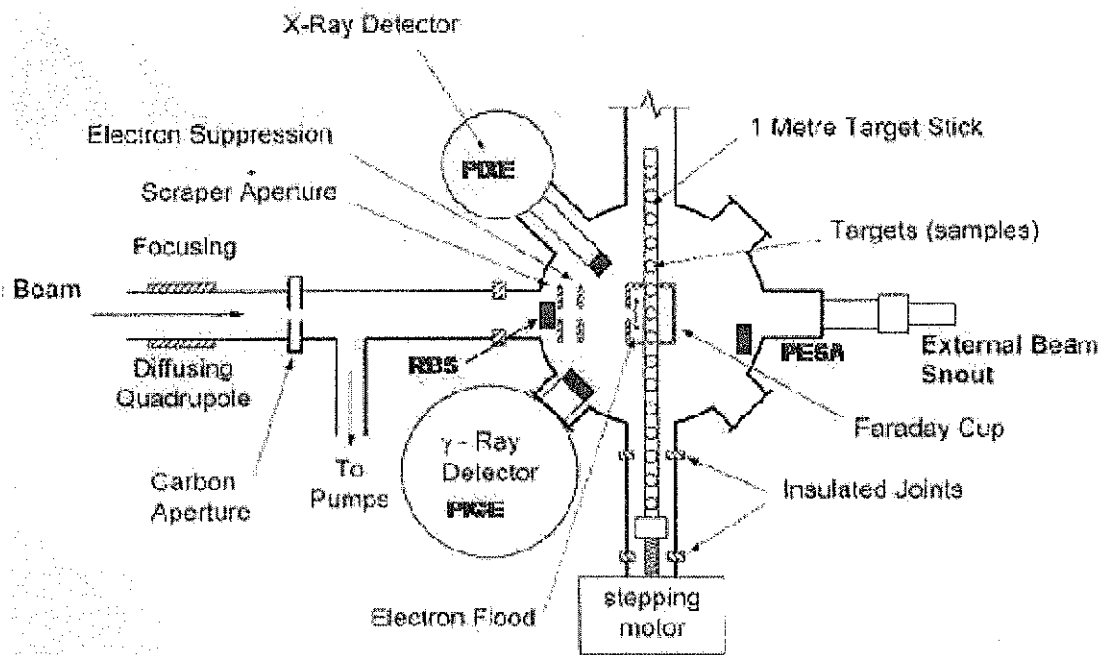
Figure 3-6-1 Proton induced X-ray emission.

Figure 3-6-2 Schematic of equipment used for PIXE. (Adapted from ANSTO. 2002).

3-5 Secondary Ion Mass Spectroscopy

Secondary Ion Mass Spectroscopy (SIMS) is a surface analysis technique used to determine information about the surface composition of a wide range of solid surface materials. Both quantitative and qualitative measurements are possible with the SIMS technique. Quantitative measurements require a standard reference sample to calibrate the equipment. Qualitative measurements require no reference sample and can be utilised to make comparisons of relative compositions between samples. SIMS can perform an analysis of species with a possible mass range of 1-500 amu, with a resolution in mass of $\Delta M/M = 10000$. These properties make SIMS an ideal technique for determining the relative quantities of possible trace elements and trace impurities that have been deliberately introduced through doping in the surface or near surface layers of solid surface materials.[8]

SIMS works by accelerating, collimating, and focussing a beam of ions called the primary beam onto a sample. The ions used have energy typically in the order of 100-10,000 eV. This quantity of energy is used to sputter atoms and molecules from the surface of the samples being examined, as shown in Figure 3-7-1.
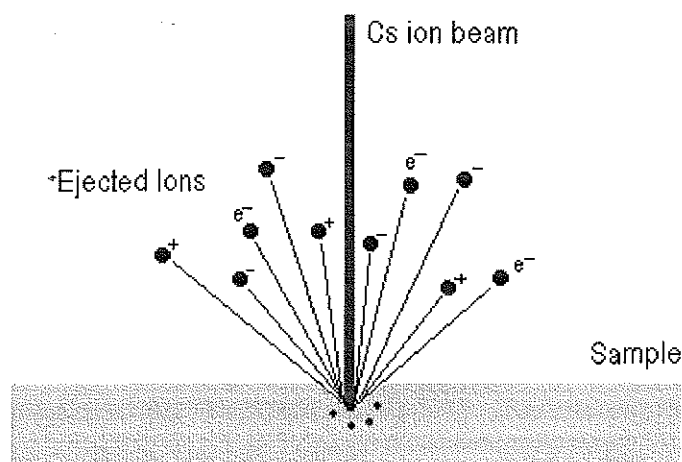
Figure 3-7-1 Cs ion beam and ejected sample ions.

This examination technique is quite destructive to the surface of the sample. In fact, there will be no film left at the spot being probed when the SIMS analysis is complete. The range of ejected particles have a number of states extending from a positive charge, to neutral, to a negative charge. Those particles present with a charge are called secondary ions. These ions are channeled through a column and measured with a mass

spectrometer (Burke et al, 2002). The information concerning the collected ions mass and charge are then sent to a computer workstation where it can be collected, stored and manipulated as needed.

Typical SIMS has a spatial resolution of 2-5μm, a depth resolution of 1-2nm, and a detection limit in the range of parts per million to parts per billion. Depth profiling is possible to a depth of up to 10μm and elemental mapping of areas up to $500 \times 500 \mu m^2$ (Burke et al, 2002).

3-6 Evironmental Scanning Electron Microscopy

The Environmental Scanning Electron Microscope (ESEM) is a Variable Pressure type Scanning Electron Microscope (VP_SEM). This means that the pressure in the analysis chamber is dynamic, it can be changed. This type of microscope can accommodate several different types of detectors such as Secondary Electron Detectors and Back Scattered Electron Detectors. The microscope incorporates several pressure limiting apertures that keep the pressure in the column constant while allowing the pressure in the chamber to be changed (see Figure 3-8-1). An important difference between this type of microscope and a normal SEM is that insulating as well as conducting samples can be viewed without applying a conducting coating (Griffin, 2001).
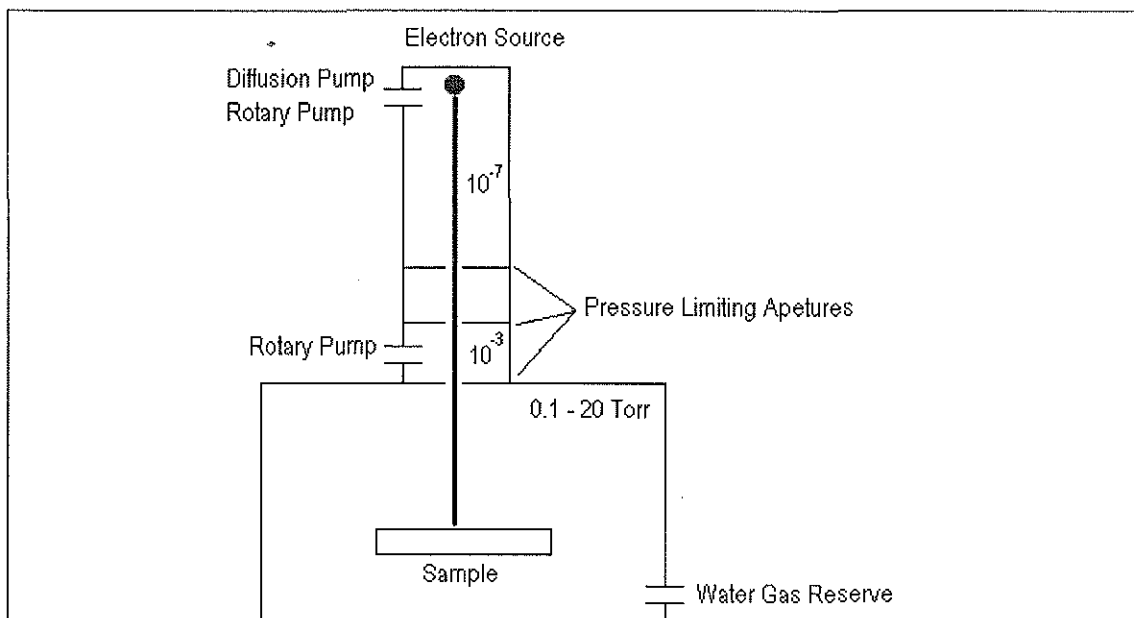
Figure 3-8-1 ESEM vacuum system design (adapted from Griffin, 2001).

3-6-1 Secondary Electron Detector

Conventional Secondary Electron Detectors can not be used in a VP_SEM. The relatively high pressure of gas in the analysis chamber, combined with the scintillator bias, causes arcing. Instead, the Danilatos model is used where a positively charged detector attracts a signal. The signal is amplified by a reaction between the secondary electrons and the gas particles that causes an electron cascade. The charge created on the sample by the primary electron beam is cancelled by the flood of positive ions created by the interaction of the secondary electrons with the gas (Griffin, 2001). This process is shown in Figure 3-8-2.
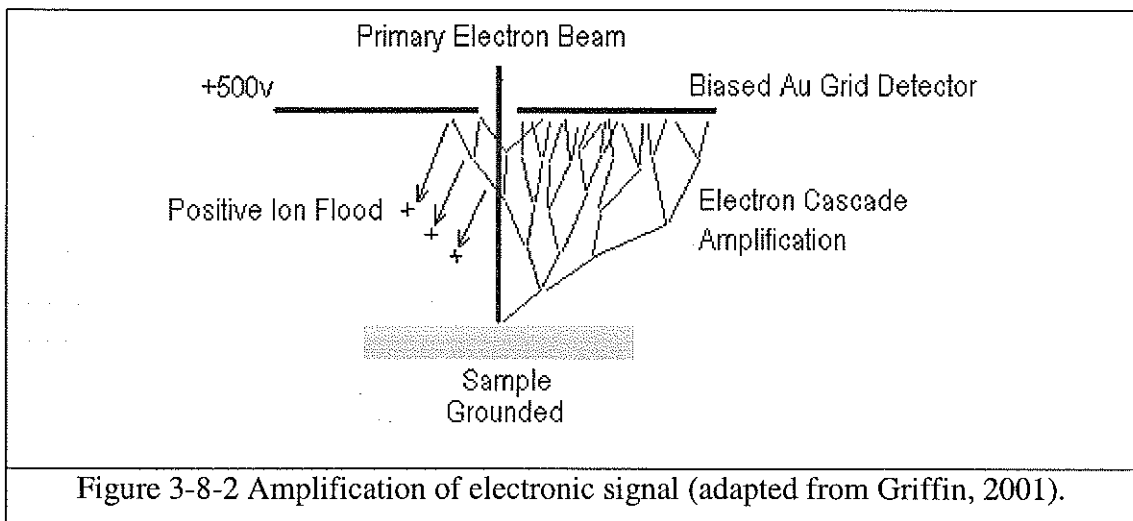
Figure 3-8-2 Amplification of electronic signal (adapted from Griffin, 2001).

3-7 Charge Contrast Imaging

Charge Contrast Imaging (CCI) is brought about by charging effects that manifest themselves as differences in contrast in an image. CCI has applications in material imaging, defect imaging, and in examining film contaminates and defects. Information gained from CCI exhibits a close correlation with that gained from Cathodoluminescence. It should be noted that conventional coating of samples with conducting layers such as Gold and Carbon is not required and will in fact prevent imaging via the CCI technique.

There are a number of problems associated with CCI. Firstly, the surface of the material can experience some contamination during analysis. Secondly, the primary electron beam will experience some scattering which can lead to a reduced spatial resolution.

The contrast in a CCI image is stable at constant operating conditions and is reproducible. However there are a few factors that the system can be sensitive to, such as electron beam current, chamber pressure, PLA size, scan rate, working distance, and ESD grid bias. The system is also found to be relatively impartial to the accelerating voltage, although it can have a small effect on the contrast in the image and the surface state, whether it be polished, scratched, or cracked.

Optimum conditions can be obtained for examining most samples, however, if the chamber pressure is too high, the contrast in the image will convert back to the conventional Secondary Electron detail. If the chamber pressure is too low, the contrast in the image will convert to a surface charging effect. It is useful to compare the images obtained from the CCI process and that of the normal Secondary Electron (SE) process. The primary difference observed when comparing a CCI and a SE image is the decreased resolution in the CCI. This is a product of having a higher pressure in the analysis chamber in the VP_SEM. Despite the decreased resolution, the CCI process is still extremely useful as it can view insulating samples that the SE process cannot, and can differentiate regions of the sample by their charge content. This should make CCI ideal for imaging semiconductor materials and devices (Gluszak & Hinckley, 2001; Griffin, 2001).

MATERIALS AND METHOD

4-1 Chemical Bath Deposition

The Chemical Bath Deposition (CBD) process is one of the simplest and cheapest processes with which to create thin film structures such as CdS thin films. The CBD process basically involves the submersion of substrates in a solution containing a chemical system that will deposit a film onto the substrate surface. The entire process revolves around the composition of the chemical bath. The constituents of the chemical bath create a precipitate that deposits on the substrates. Various aspects of the process such as temperature, concentration of the various chemical constituents, and deposition time can be manipulated to control the characteristics of the deposited thin film.

4-1-1 Background

Former student Edward A. Gluszak designed the first apparatus in 1996 (Gluszak, 1996), shown in Figure 4-1-1-1. The apparatus incorporates a water bath heated by a 500ml electrothermal heating mantle, a thermocouple temperature controller linked to the heating mantle, and an electric motor with stirrer connected to a ceiling fan controller for speed control. Substrates are held in place in a 250ml beaker which is used as the reaction vessel in the water bath.
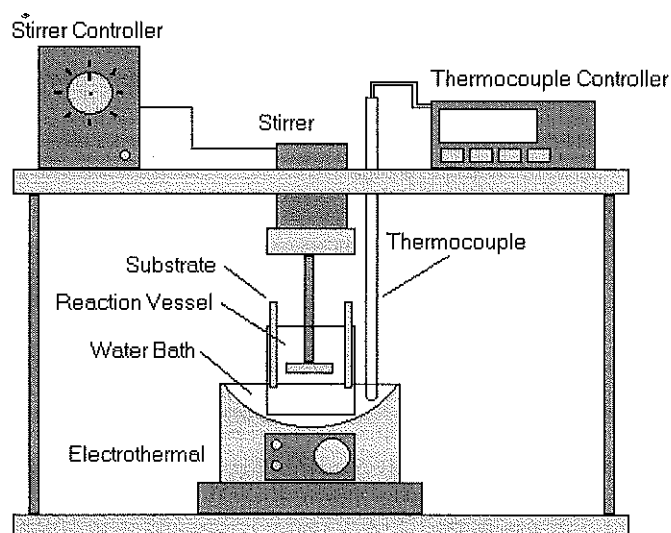

Figure 4-1-1-1 Edward Gluszak's Experimental Apparatus (adapted from Gluszak, 1996).

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This experimental apparatus, as functional as it is, has several areas that needed development to increase its efficiency and ease of operation. First, the reaction chamber, reagents and slides are open to the outside system. This poses two problems, possible contamination with outside particulate sources and thermal instability. Since the system is open, thermal energy can easily escape, which in turn provides problems when trying to maintain a constant reaction temperature. Enclosing the reaction vessel in polystyrene and foam can easily solve this problem. This closes the system off from any contaminants and prevents most of the thermal energy from escaping. Second, the stirring device, although very efficient, is providing a path for thermal energy to escape as it is made of metal. This device was replaced with a magnetic stirrer and magnetic flea. The magnetic stirrer, also being more appropriately designed for the task, provides more control over the state of agitation in the reaction vessel. Finally, with the reaction vessel enclosed in polystyrene, the electrothermal heating mantle is no longer useful as it would melt the polystyrene. For this reason it is replaced with heating coils inside the polystyrene jacket and a preheating stage in the production process for reagents.

4-1-2 Current Experimental Apparatus

The experimental apparatus used in this study is shown in Figure 4-1-2-1, and consists of an 800ml beaker wound with coils of wire that are connected to an IEC CAT No 2633-001 DC power supply. The coils are not used to heat the contents from room temperature. Instead, reagents are preheated then transferred to the reaction chamber. The coils are then used to maintain an appropriate temperature. However the heating coils can be used to increase the temperature by small amounts, although temperature increases of anything more than 5 or 10 degrees Celsius take too long, as the heating coils are not very powerful. The beaker has several layers of cell air foam wrapped around it and is inserted into a polystyrene jacket. The jacket has an inner and outer lid that seal shut during the operation of the system. Encasing the reaction chamber in insulating foam prevents the heat from escaping so that only small amounts of energy are required to maintain the temperature of the reaction system. Situated in the lid is a plug that allows for easy access to substrate slides and thermocouple. This also allows for the addition of chemical reagents. The type-T thermocouple is connected to a BC BTC-2220 thermocouple controller which is linked to the power supply for the purpose of monitoring and controlling the temperature. The whole system is then situated on an IEC CAT No 76083v hot plate-stirrer. No heat is required from the hotplate, and the

magnetic stirrer is used to sufficiently agitate the reagents throughout the whole process. This ensures that the chemical reagents remain uniformly mixed and provides an even deposition on the substrates.
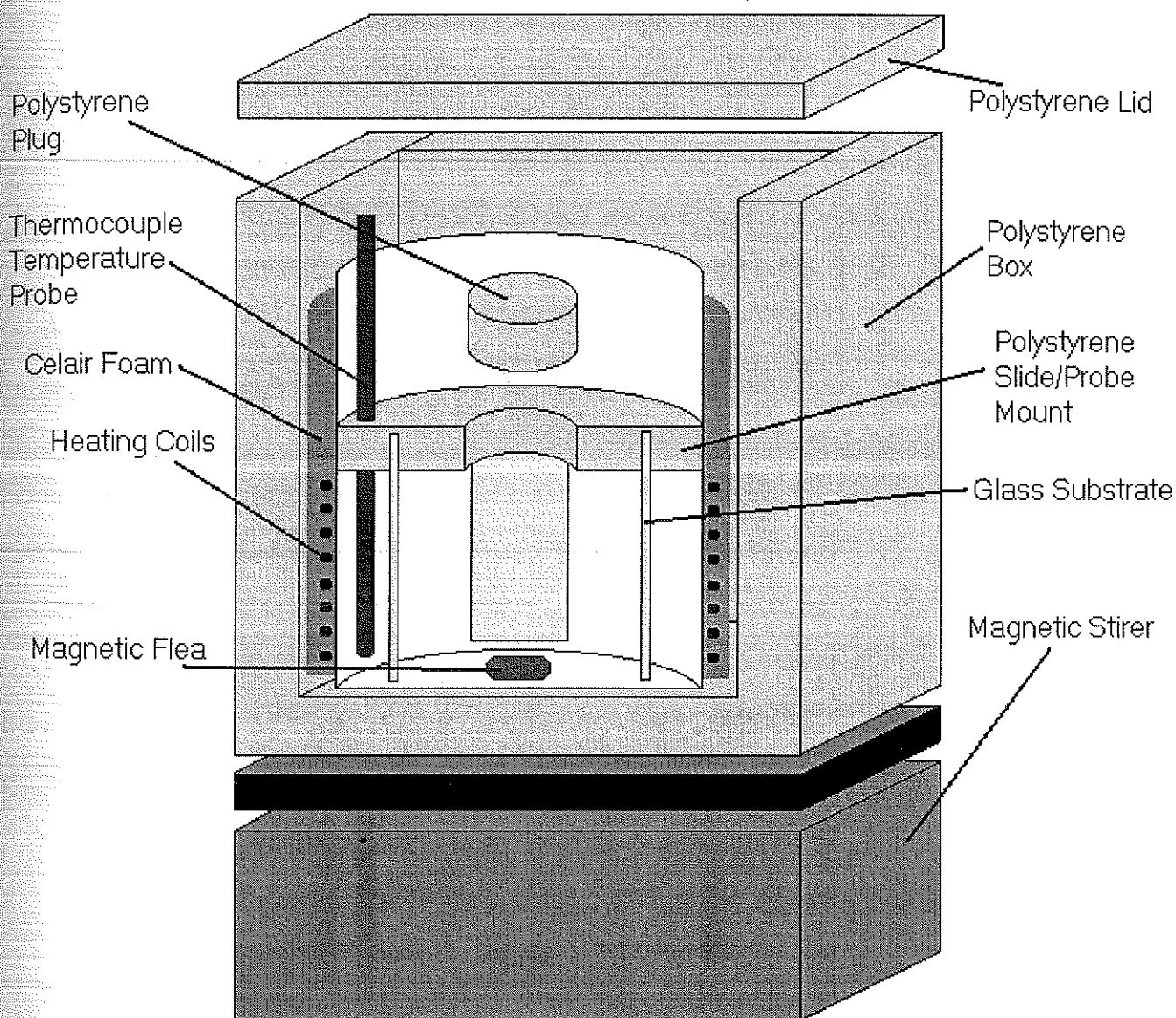
Figure 4-1-2-1 Experimental Apparatus used to deposit films in this study.

4-1-3 Experimental Technique

The technique employed to produce the thin films is quite simple. Firstly the hot plate, power pack, thermocouple and reaction chamber are set up. The reaction chamber and thermocouple are then cleaned with a concentrated sulfuric acid solution to remove any contaminants, and then rinsed with Milli-Q water. The substrates onto which the film will be deposited are cleaned in a bath of concentrated sulfuric acid for 30 minutes, then

rinsed in Milli-Q water and positioned in their holder to be placed into the reaction chamber. The substrates were standard glass microscope slides. An optimum concentration of the CBD constituents was predetermined from previous work and stock solutions were prepared. 350 mL of Milli-Q water is then preheated to $10°C$ above the determined reaction chamber temperature, the water is added directly to the reaction chamber and the heating coils engaged. 42 mL of 17 ML^{-1} ammonia solution is then added to the system and is allowed to equilibrate for 10 minutes. When the desired reaction chamber temperature is reached, 4 mL of 0.2 ML^{-1} Cadmium Acetate Dihydrate $(Cd(CH_3COO)_2.2H_2O)$ stock solution reagent is added, and the system is again allowed to equilibrate for 5 minutes. Finally 4mL of 0.4 ML^{-1} Thiourea (H_2NCSNH_2) stock solution reagent is added, the reaction chamber is then closed up and deposition time begins. Some of the films had Indium dopant, which was accomplished by adding a very small volume (<2mL) of Indium III Chloride Tetrahydrate $(InCl_3.4H_2O)$ 0.004 ML^{-1} stock solution just after adding the Cadmium Acetate Dihydrate.

4-1-4 Post Deposition Processing

Post deposition processing is a straight forward task where the slides are cleaned, and if need be, annealed. When the deposition is completed, the substrate slides are extracted carefully so as to not damage or contaminate the films, and rinsed in Milli-Q water. They are then placed in an ultra-sonic cleaner with Milli-Q water for 30 minutes. The slides are then removed, rinsed with more Milli-Q water, and allowed to dry in air. Depending on the desired characteristics of the films, annealing was conducted. The slides are placed in stainless steel racks and put into an Analite Model 4 furnace at an optimum temperature of $400°C$ for a period of 60 minutes, with an air atmosphere. An air atmosphere was chosen because the Oxygen is substituted for the Sulfur in the CdS lattice, which has the effect of increasing the n-type nature of the thin film and enhancing the conductivity. When the annealing process is completed the slides are extracted and allowed to cool slowly in air. The cooled the slides can then be cut with a straight edge and glass cutter to sizes more appropriate to experimentation. Special care is taken not to contaminate the slides with finger prints or latex while cutting.

4-2 Secondary Ion Mass Spectroscopy

SIMS measurements were performed at the Australian Nuclear Science and Technology Organisation (ANSTO) under a grant from the Australian Institute of Nuclear Science Engineering (AINSE). The SIMS used was a Cameca brand ims5f magnetic grid SIMS. This was interfaced with a Sun Microsystems computer used to capture and process data.

4-2-1 Sample Preparation

The slides produced in the Chemical Bath Deposition are too large to mount in the analytical chamber of the SIMS. The samples therefore have to be cut down significantly. A number of samples can be mounted at one time on a number of different mounts. These mounts are the same size but have different viewing window configurations of 3, 9, 14 and 18 requiring increasingly smaller sample sizes. Glass slides are not easily cut to very small sizes so the 3 window sample mount was used. While cutting the samples to size it is important to remember to keep them as contaminant free as possible. Oily finger prints provide the most trouble as they can lead to very long pump times when evacuating the analytical chamber. Several precautions were taken to combat this. Firstly, a clean operating environment was used to process the slides. Secondly, gloves were worn to prevent the contamination of the slides with any dirt or oil. And lastly, if any contamination was present, an alcohol solution was used to clean the slide prior to mounting it. The mounting procedure is very simple, the precut samples are placed in the holder with the analytical surface down and a spring loaded backing pate is screwed on top to hold them in place. A schematic of the sample holder used can be found in Appendix C, within the sample preparation guide provided by ANSTO.

4-2-2 Analysis

The analysis of the samples was conducted with a Cs^+ source. Only the relatively thick samples provided usable results as the thin samples experienced surface charging as they were bombarded with the Cs^+ ions. The surface charging caused the analytical beam to deflect. It was also found that in the thin samples, the beam sputtered through the CdS surface to the glass very quickly and then the glass surface charge deflected the beam, also giving unreliable data. Despite these problems, useful data was acquired from a good number of slides. Several relevant elements were examined, including

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oxygen, silicon, sulfur, arsenic, cadmium and indium. The results provide a qualitative comparison of the elemental composition between the samples. To perform a quantitative analysis a standard was required to calibrate the SIMS hardware. However, no CdS or In standard samples were available at the time of analysis. Despite this good quality results were obtained for the qualitative analysis.

4-2-3 Charge Compensation

To compensate for the charging on the surface of the very thin samples, two techniques were employed. A gold coating was applied to the surface of the sample using a gold sputter coater. This functions to improve the conductivity near the surface of the sample so charge that builds up where the analytical beam hits the sample surface can be dissipated more quickly. The second technique is to use an electron gun focused at the area being examined to compensate for the charge buildup. This technique was employed to examine a variety of the thinner more troublesome samples with and without gold coatings, however, the quality of result achieved was still far from acceptable.

4-3 Atomic Force Microscopy

AFM measurements were conducted at ANSTO under a grant from AINSE. At the time PIXE measurements were to be carried out, however, this equipment was unavailable, as a result time with the AFM was supplied as a temporary substitute. The type of AFM used was a Digital Instruments Nanoscope IIIa.

4-3-1 Analysis

The analysis of the samples was conducted in the contact mode of operation. Firstly, a suitable area of film was selected that had a consistent coating of CdS. Then images were taken at sizes of 50, 10, and 5μm. When the AFM had finished compiling the image into a tiff file it was flattened to remove any tilt brought about by uneven orientation of the sample when it was mounted and again saved as a tiff file. The flattened images were later examined with the off line software supplied by Digital Instruments. The off line software required a Pentium computer with Microsoft Windows NT 4.0 operating system installed. Three dimensional plots of the surface were then constructed.

4-4 Charge Contrast Imaging

CCI images were taken at the Centre for Microscopy and Microanalysis at the University of Western Australia (UWA) using an Electroscan Environmental Scanning Electron Microscope. The use of the facilities at UWA were facilitated via the Western Australian Centre for Microscopy (WACM) agreement.

4-4-1 Sample Preparation

Unlike other SEM's, the ESEM requires very little sample preparation. Usually samples that have a high resistivity such as CdS are required to have a conductive coating such as carbon or gold. However, this is not needed due to the ESEM's unique operating conditions. Slides were required to be cut to a small size to fit on the stage approximately 2cm square or smaller. Samples were then adhered to the stage with carbon tape.

4-4-2 Analysis

Analysis of the CdS thin films was conducted at a relatively low chamber pressure of between 1.5 and 3 Torr and the medium sized bullet aperture was used. The accelerating potential was set to the highest setting available, 30keV. The working distance was set to approximately 5mm to provide a good resolution at higher magnifications. A spot size of 30 was also selected which means only 30% of the analysis beam was wasted. A secondary electron detector was used to measure the electrons that were emitted. Once a suitable image was acquired it was sent to a computer that captured them and saved the images as tiff files. The images could than be transferred to the image analysis lab and manipulated to maximise the detail quality.

4-5 Proton Induced X-ray Emission

PIXE measurements were conducted at ANSTO under a grant from AINSE using the SR-2 3MV accelerator facility. At the time PIXE measurements were to be carried out, however, this equipment was unavailable, as a result staff at the ANSTO facility were supplied with a selection of samples to be examined at a later date.

4-5-1 Analysis

Samples such as the CdS thin films require no sample preparation for examination with PIXE. The samples are simply mounted on a sixty sample slide and the equipment is set to automatically test each one. The X-ray lines for each of the elements Sulfur, Cadmium and Indium were examined to determine their concentrations in the thin films. The determination of the concentrations of Cadmium and Indium was done using the L X-ray lines which happen to overlap. Along with beam stability problems, this has resulted in some anomalous values due to the analysis software being unable to resolve the interference.

4-6 Electrical Measurements

Electrical measurements were carried out using a simple series resistance circuit and a multimeter. A 1.5 V battery and 30 MΩ resistor were connected in series with the CdS thin films. The CdS thin film was contacted to the circuit with Indium to ensure an ohmic connection. The distance between the two conections on the CdS thin film was 10mm. The potential across the 30 MΩ resistor was then measured with a Hewlett-Packard 34401A Multimeter. A schematic of the circuit is shown in Figure 4-6-1.
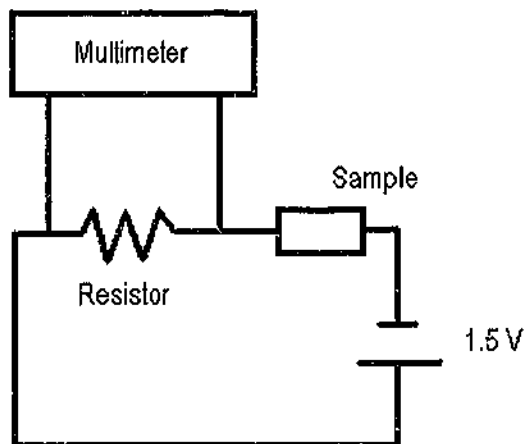
Figure 4-6-1 Circuit used for electrical measurements.

4-6-1 Analysis

In analysing the CdS thin films, two measurements were taken of the potential across the 30 MΩ resistor with the sample in the dark and under light sources. The CdS sample

was illuminated with two different light sources, a flash light and strobe which is much more powerful. This was to give an idea of the effect of different amounts of illumination. Once the information was gathered the resistance for the sample could be calculated using Ohm's Law:

$$V = IR \qquad\qquad [4\text{-}6\text{-}1\text{-}1]$$

The objective here is to compare the conductive properties between samples, and in the dark and under illumination. This is just a qualitative analysis, not quantitative one.

RESULTS

5-1 Chemical Bath Deposition

A variety of slide deposition conditions were used and samples were grown using the CBD method. Several variables were altered to produce an even spread of electrical, optical and compositional properties to examine. Table 4-1-1 below identifies each sample with its deposition conditions.

Table 4-1-1 Table of sample deposition conditions.

Sample	Deposition Temperature (°C)	Indium Dopant Concentration In Deposition Solution (%)
04A,B,C	60	0
04D,E,F	60	0
05A,B,C	70	0
05D,E,F	70	0
06A,B,C	80	0
06D,E,F	80	0
07A,B,C	60	1
07D,E,F	60	1
08A,B,C	70	1
08D,E,F	70	1
09A,B,C	80	1
09D,E,F	80	1
10A,B,C	60	0.1
10D,E,F	60	0.1
11A,B,C	70	0.1
11D,E,F	70	0.1
12A,B,C	80	0.1
12D,E,F	80	0.1
13A,B,C	60	0.01
13D,E,F	60	0.01
14A,B,C	70	0.01
14D,E,F	70	0.01
15A,B,C	80	0.01
15D,E,F	80	0.01

The Cadmium Acetate, Thiourea, and Ammonia concentrations were kept constant at 2mM/L, 4mM/L, and 1.8M/L respectively. The reaction chamber temperature, and Indium concentration were the two main variables of concern. Four reaction chamber Indium concentrations of 0%, 0.01%, 0.1% and 1% were chosen in conjunctions with

three reaction temperatures of 60, 70 and 80°C. This provided a range of 12 different slide compositions and production conditions. Six of each slide were manufactured providing seventy two slides in total. Half of each type of slide, those labeled A,B, and C was then annealed in air which in turn provided twenty four different slides each in triplicate to allow for different testing requirements.

5-2 Visual Analysis

The reaction chamber temperature seemed to have a direct effect on the surface characteristics. Shown in Figure 5-2-1 are three samples that are as-deposited with 0% Indium doping, produced at 60, 70 and 80°C.

Figure 5-2-1 As Deposited CdS Thin Films with 0% Indium doping.
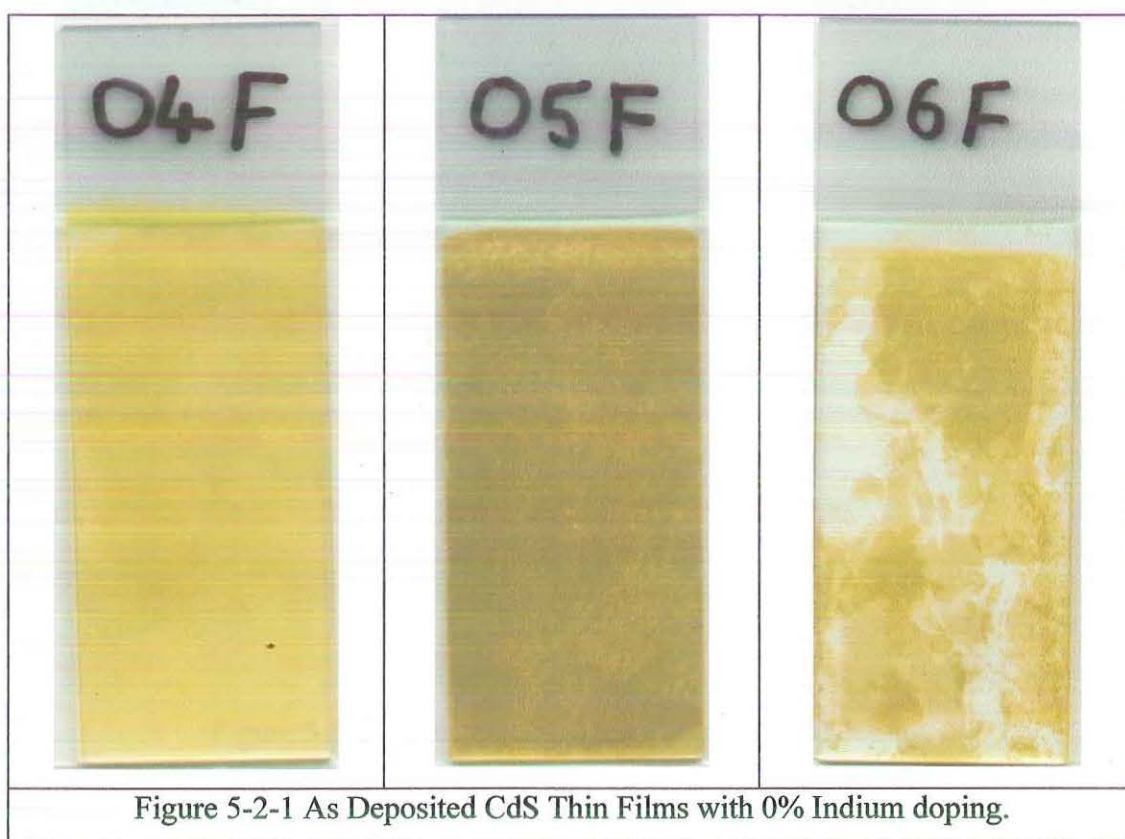
As can be seen from a visual inspection, the slide labeled 04F produced at 60°C has a relatively even coating of CdS. Slide 05F produced at 70°C appears much darker which suggests a much thicker coating of CdS and the coverage of the slide is still relatively even. Slide 06F has a slightly darker appearance than 04F but not as dark as 05F, indicating a thickness somewhere in between. However it is worth noting that the coverage of CdS is poor at best with large areas having no deposit at all. This can be attributed to the change in dominance of the two systems by which CdS is being

formed. During the deposition there is an ion by ion deposition and a particulate formation taking place. The ion by ion deposition produces the desired smooth crystalline deposits on the substrates, and the particulates are formed in the solution. At higher temperatures the CBD system was observed to favour the formation of particulates, so that there are less reactants left for the ion by ion deposition.

The annealing process also had a marked effect on the visual appearance of the slides. Shown in Figure 5-2-2 are slides from the same subset as above only they are annealed.
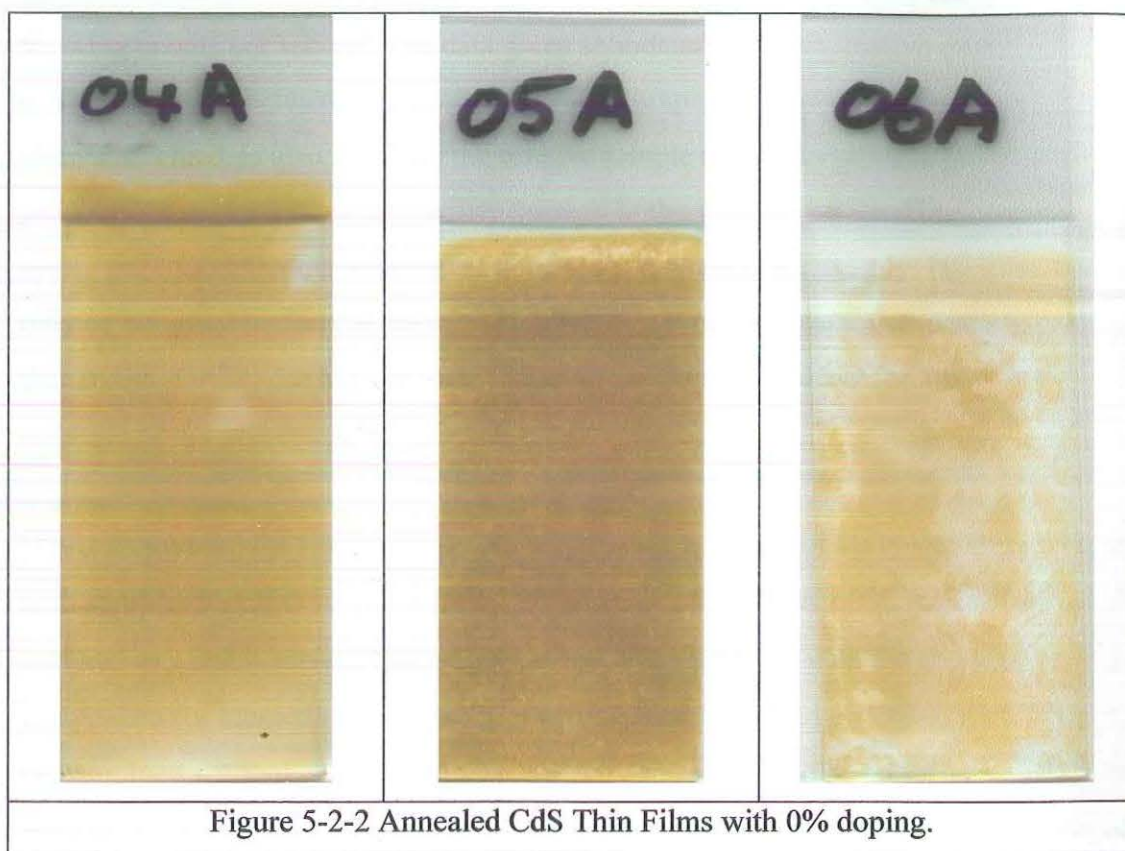
Figure 5-2-2 Annealed CdS Thin Films with 0% doping.

It can plainly be seen here that the coverage of cadmium sulfide is the same as in the as-deposited counterparts, only the color of the film has changed quite significantly. Instead of a yellow brown we have a very distinct orange brown color. This can be attributed to the change in elements and compounds present. Sulfur present on the substrate has a yellow colour, this element can be diffused out of the film in the annealing process. This decreases the intensity of the yellow colour in the films. During the annealing process oxygen is diffused into the film which may combine with the Cadmium to form Cadmium(II) Oxide which has a brown colour. These two factors

combined with Cadmium Sulfides yellow-orange colour turn a yellow orange as-deposited film into an orange brown annealed film.

5-3 Secondary Ion Mass Spectroscopy

The SIMS data was organised in an ASCII text file in the form of a depth profile. The data gives information on the relative quantities of elements present with respect to the probing depth. Files from the SIMS computer include a summary of the operating conditions and two columns of data for each element, one for the time and the other showing counts per second. The data gives an indication of the relative quantities of elements present between samples, however a comparison can not be made between elements. The data also indicates the relative sample thickness between samples as a product of how long it took to sputter through to the glass substrate. This is indicated where the concentration of elements present starts to drop off sharply. However, this is only of marginal interest as only a very select range of samples was examined .The raw data in the ASCII files has been converted into a graphical format for analysis. An example of the raw data can be found in Appendix B.

While examining the films with the SIMS technique, some difficulty was experienced with samples that had very thin films. Those films produced at 60°C were exceptionally thin and as a result surface charging occurred, this interfered with the acquisition of any usable data for these slides. Those films produced at 80°C had a suitably thick film to be examined without charging, but were patchy so care had to be taken in selecting an appropriate area for examination. Films produced at 70°C had a consistent covering of the slide and were of an appropriate thickness to avoid any charging complications. For this reason the analysis has concentrated on the films produced at 70°C.

An analysis of graphical data reveals many relevant details concerning the annealing and doping of the CdS films, as well as trace impurities and relative film thickness. A comparison of the annealed samples 05C, 08C, 11C and 15C with the as-deposited samples 05D, 08D, 11D and 15D shows there is approximately 10 times the quantity of Oxygen present in the annealed samples. This indicates that during the post deposition processing when the films were annealed in air, oxygen permeated the crystal structure

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of the films. The quantities of Cadmium and Sulfur present in both the annealed and as-deposited samples is very similar. This can be seen in Figures 5-3-1 through 5-3-8.

By making a comparison of the graphical data, the effect of Indium doping on the CdS film composition can be seen. It is important to note that in the production of the films, the concentration of Indium in the chemical bath solution was 0% for 05C and 05D, 1.0% for 08C and 08D, 0.1% for 11C and 11D, 0.01% for 15C and 15D. Films 08C and 08D show approximately 10 times the amount of Indium present than in films 11C and 11D. Films 15C and 15D show 10 times less Indium again than that found in films 11C and 11D. However the Indium present in 11C and 11D is so low that it would be very difficult to distinguish it from the levels present in films 05C and 05D, which have only trace impurities present.

It is also worthwhile to note that the concentration of Indium in the films varies as a function of depth. The concentration of Indium increases as you probe deeper into the film. This is likely due to the concentration of Indium in the chemical bath solution decreasing as it is used up in being deposited on the substrates. It can be determined from Figure 5-3-9, a plot of the Indium concentrations in the different samples, that the annealed films tend to have slightly higher concentrations of Indium present. The SIMS results do not show any difference in the distribution of Indium as a function of depth in the annealed as compared to the as-deposited films. From the data it can also be seen that there are trace amounts of Arsenic present in the films. This is most probably due to Arsenic trace impurities present within the Cadmium reagent.
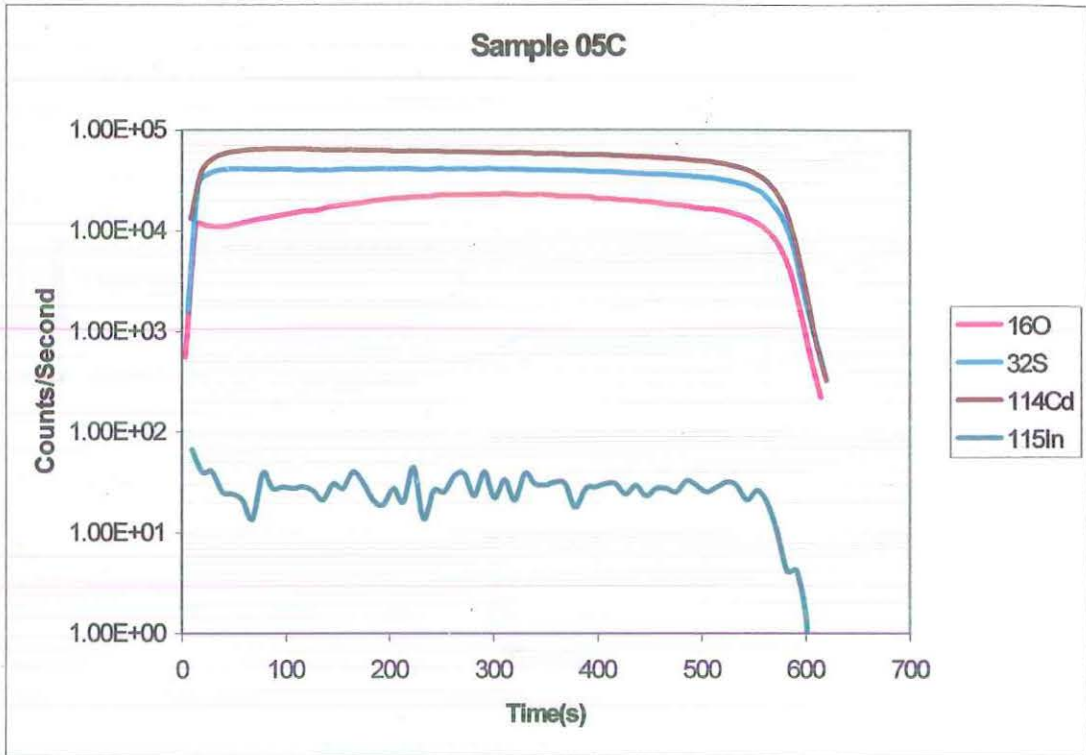
Figure 5-3-1 SIMS for sample 05C.
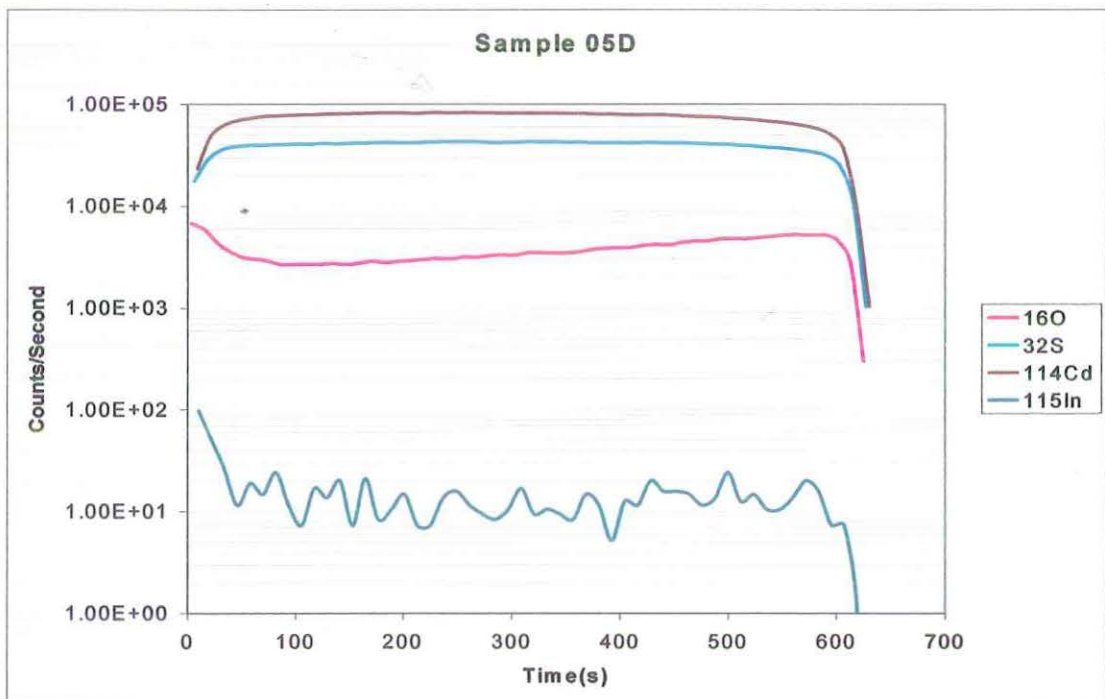
Figure 5-3-2 SIMS for sample 05D.
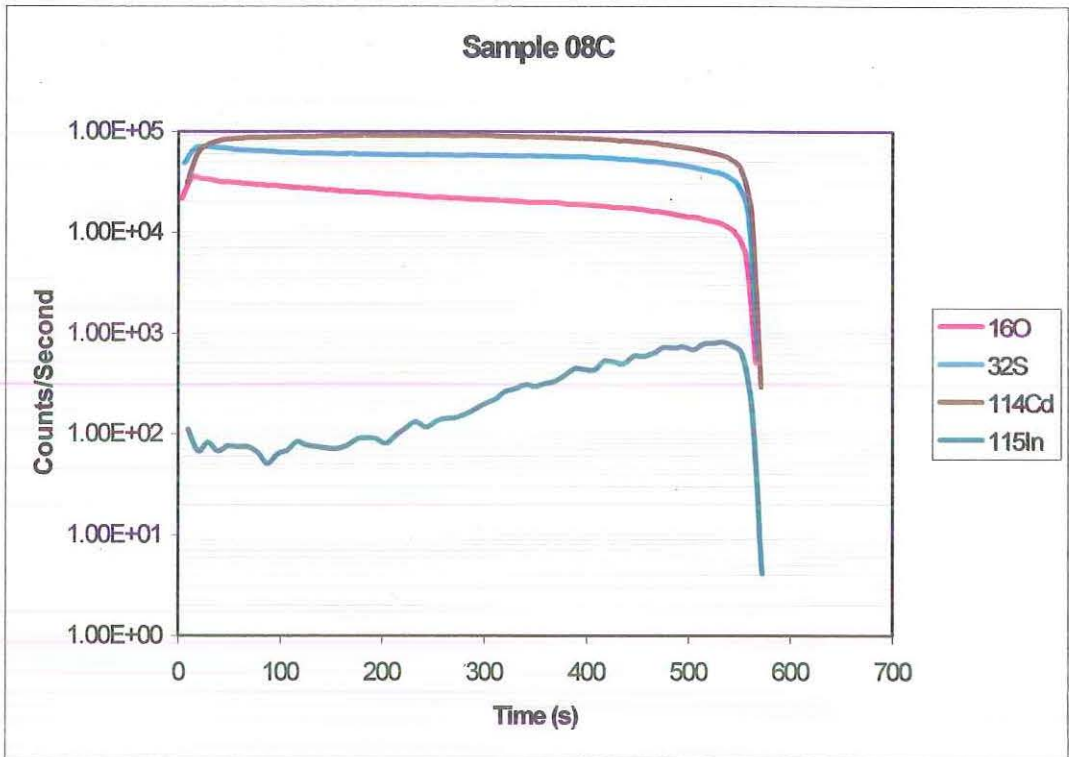
Figure 5-3-3 SIMS for sample 08C.
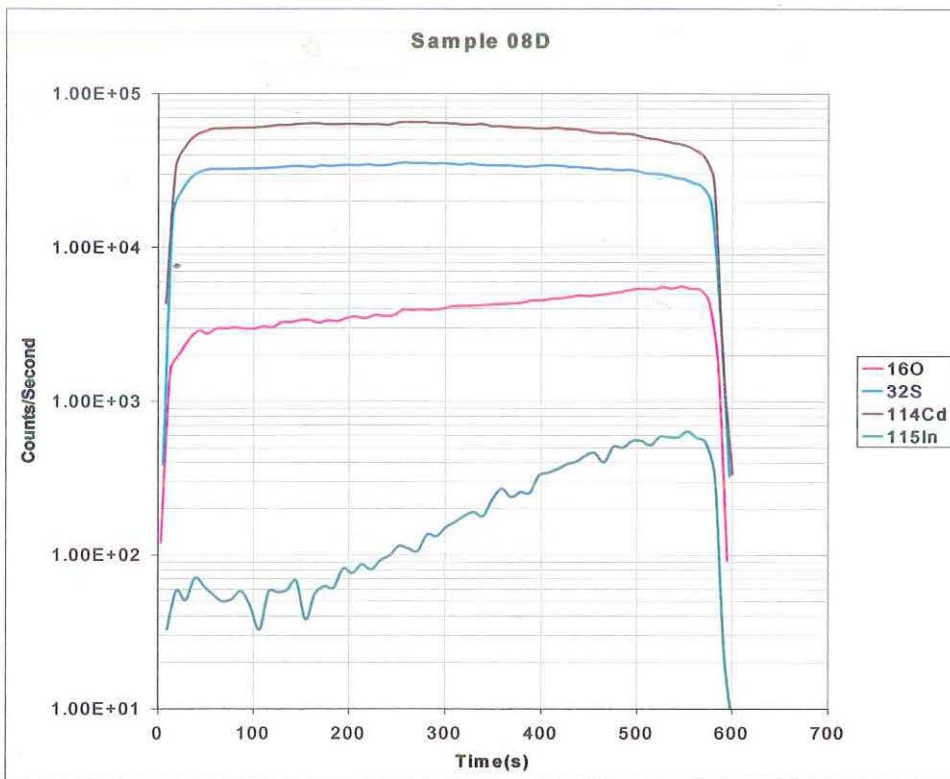
Figure 5-3-4 SIMS for sample 08D.
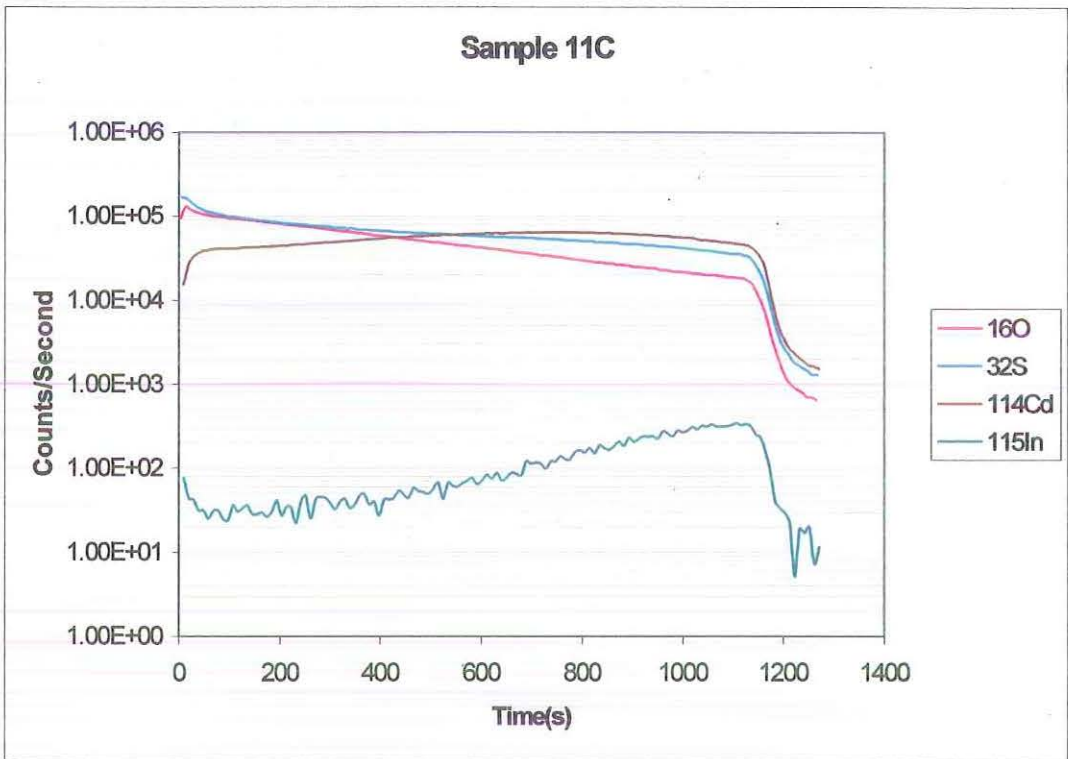
Figure 5-3-5 SIMS for sample 11C.
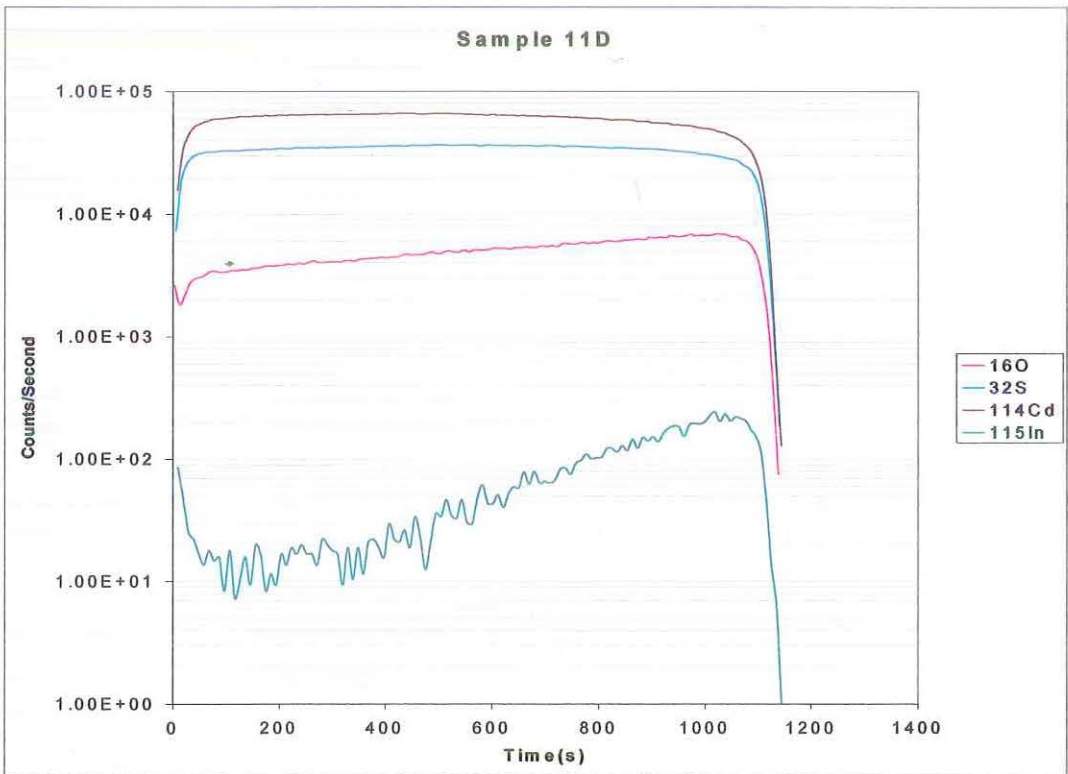
Figure 5-3-6 SIMS for sample 11D.

Figure 5-3-7 SIMS for sample 15C.
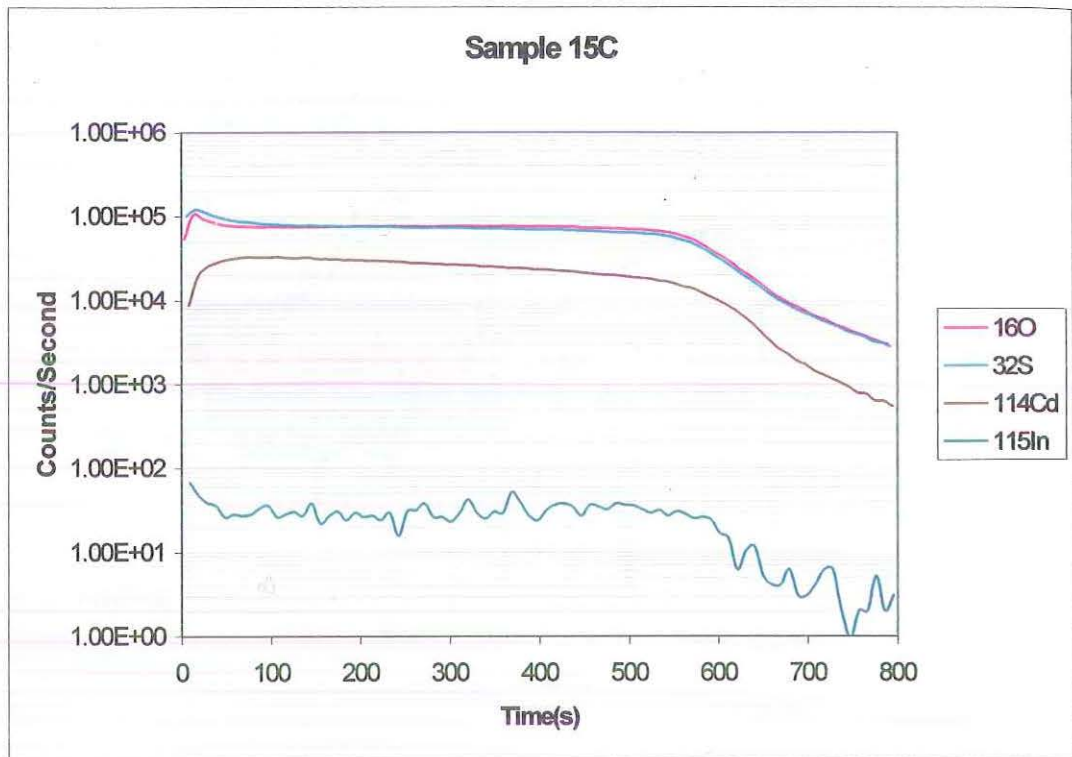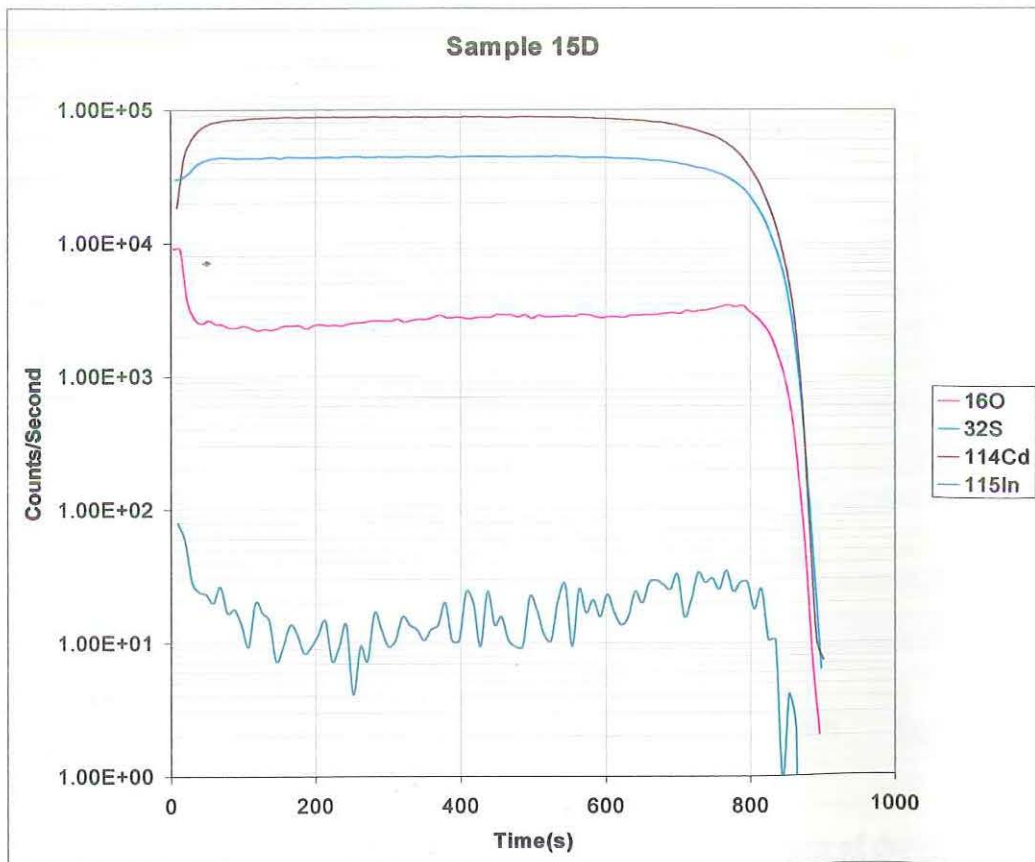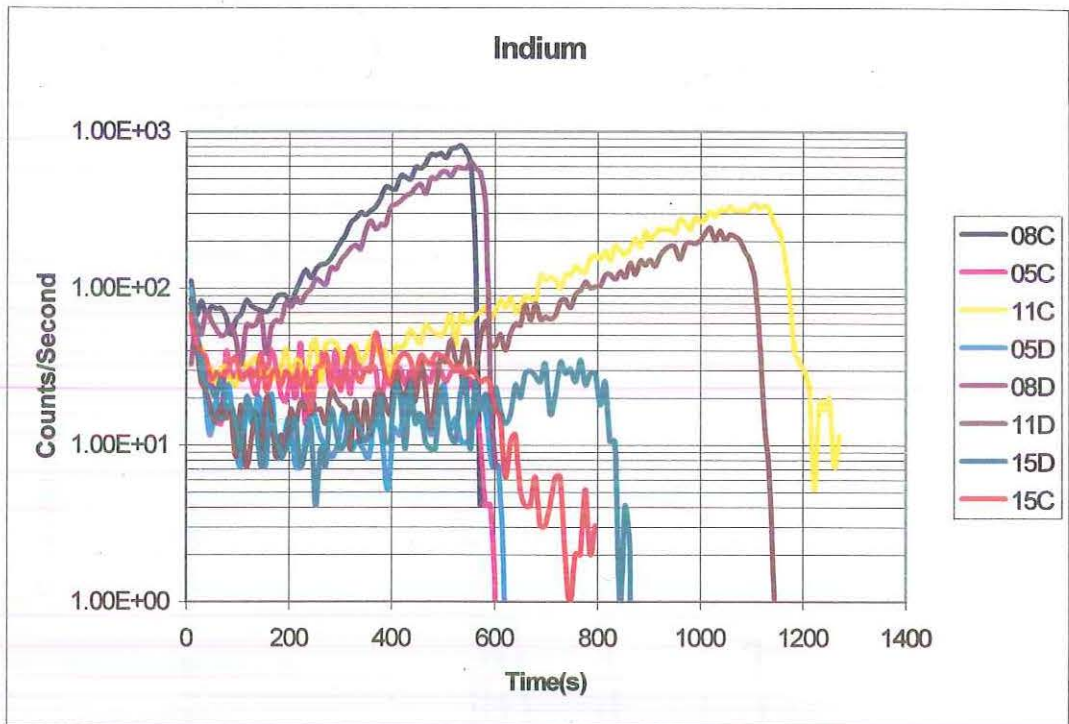

Figure 5-3-8 SIMS for sample 15D.

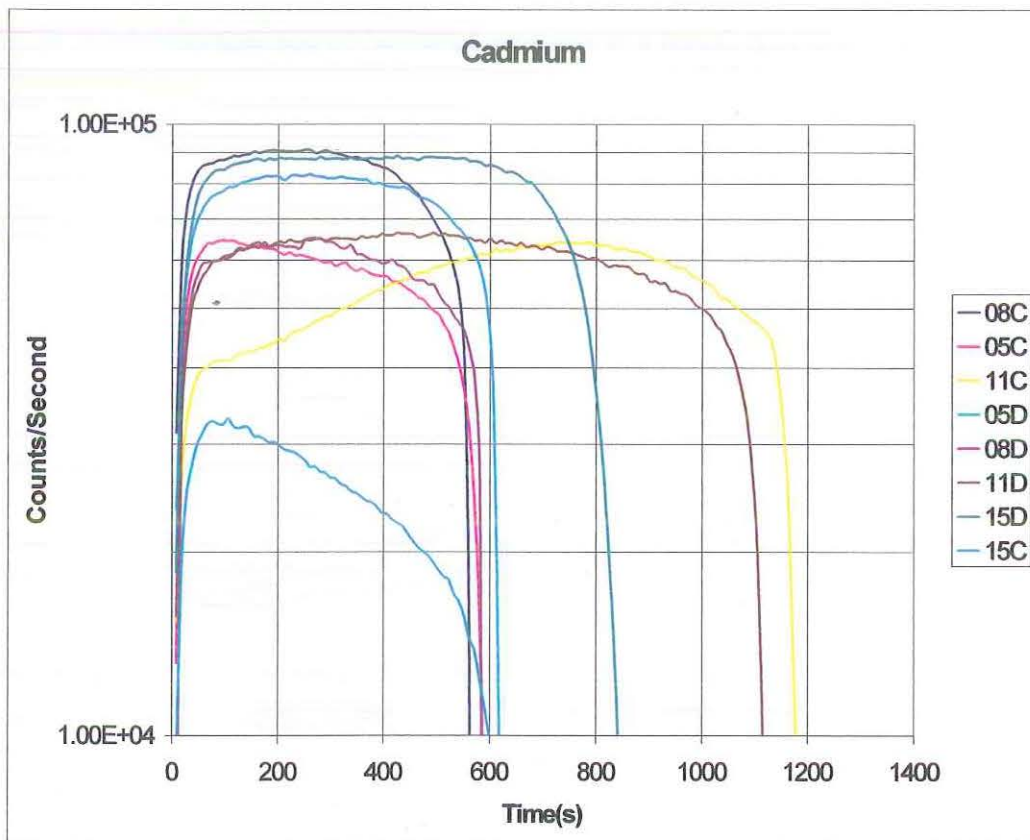Figure 5-3-9 Comparison of Indium component as a function of depth (sputter time).

Figure 5-3-10 Comparison of Cadmium component as a function of depth (sputter time).
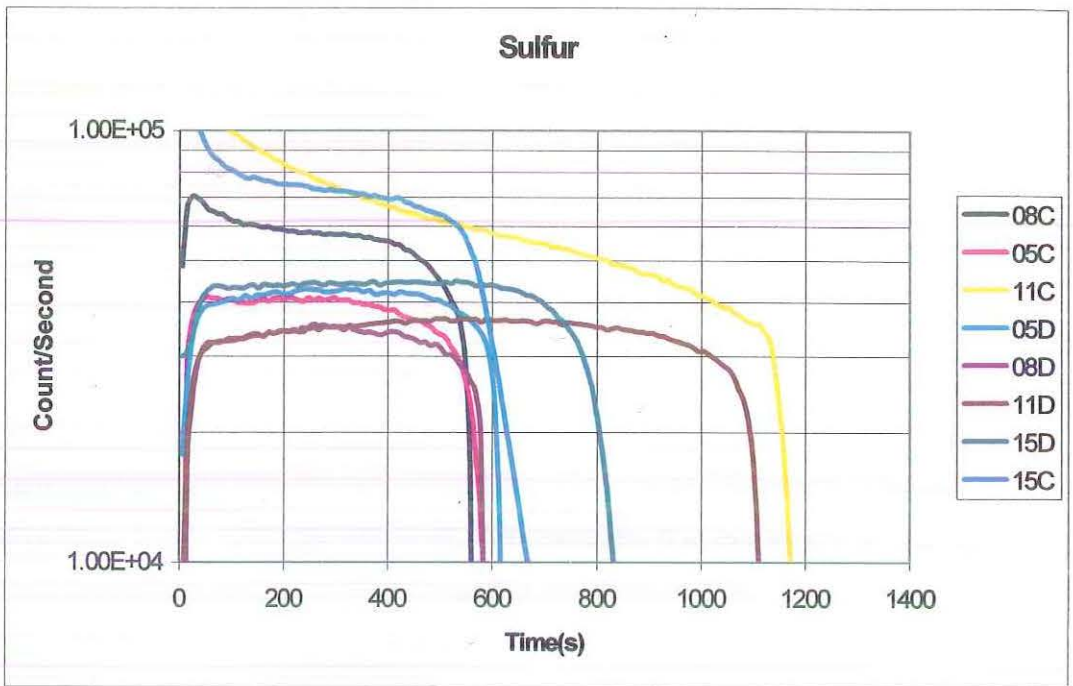
Figure 5-3-11 Comparison of Sulfur component as a function of depth (sputter time).
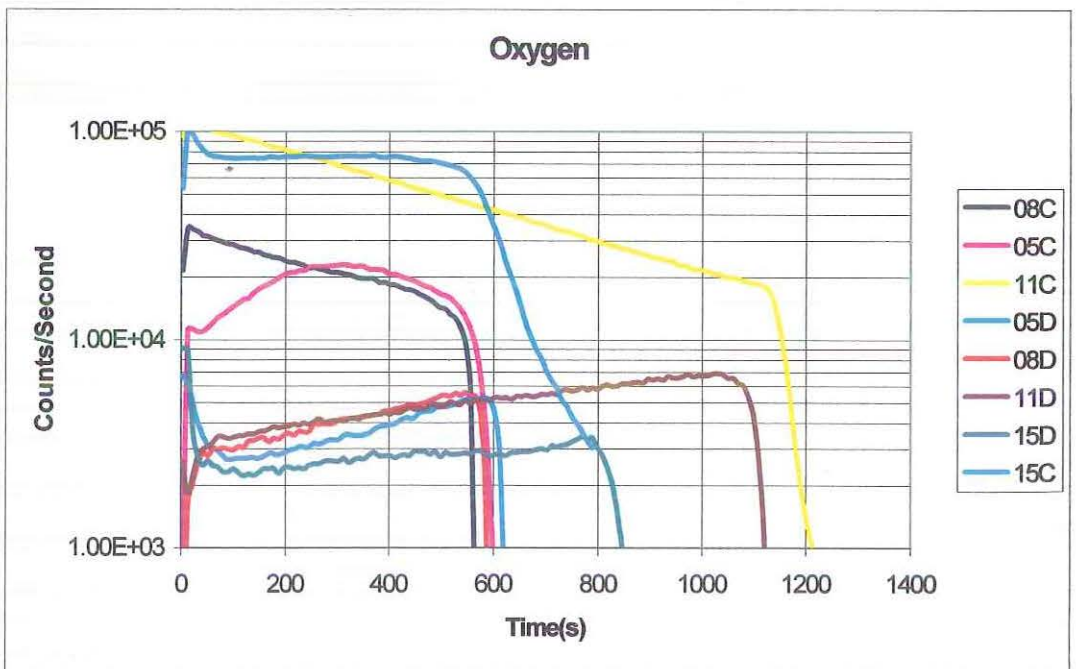
Figure 5-3-12 Comparison of Oxygen component as a function of depth (sputter time).

5-4 ESEM Charge Contrast Imaging

The CCI data was presented in the form of tiff image files. The images are in black and white and show areas of varying charge. The closer to white, the higher the charge. Surface detail can also be seen on the images. These images show the presence of different defects and structures that are present. Two images are shown for each sample, one with a relatively wide field of view and a close up.

When examining the images several important observations can be made concerning the post deposition processing of the films, and processes present during the deposition of the films. Firstly, all the annealed films have bright spots with an approximate size of 1µm covering the surface of the films. These bright spots appear to be charging significantly more than the rest of the film. The as-deposited films generally do not have these bright spots present at all. This indicates that during the annealing process some crystalline structures have formed at the surface of the film, that may have different chemical compositions to the rest of the film.

Secondly, there also appears to be small particulates present on the films surfaces that can be seen as small charging spots with irregular often jagged shapes. This would appear to be the second type of film deposition where colloidal particles of CdS adhere to the surface. An example of this can be seen in sample 07D shown in Figures 5-4-15 and 5-4-16.

Lastly, samples 06 and 09 shown in Figures 5-4-11 and 5-4-21 through to 5-4-24, which were produced at 80°C, show an inconsistent surface where not all of the glass substrate is covered. This can be seen where a smooth surface that charges differently to the rest of the film appears. Some areas of these films also show deposits of particulates stuck to the surface of the films. This indicates a decrease in the ion by ion deposition reaction, and an increase in the particulate formation. The incomplete coverage of the substrates here and in other samples shown in Figures 5-4-22, 5-4-23, 5-4-41 indicate that ion by ion deposition does not occur with sufficient frequency to cover the entire slide with an adequate film.

Figures 5-4-23 and 5-4-24 are excellent examples of the initial stages of film growth where the edge of the thin film is still growing and has not yet joined to close gaps over the substrate. Figure 5-4-5 shows the contrast effect of two different phases in the CdS thin film, one as Grey surface with white dots and the other a brilliant white patch. An excellent example of a short circuit effect can be seen in Figure 5-4-19 where a scratch in the surface of the film is preventing the charge in the film from dissipating into the right side of the image.

Figure 5-4-1 Sample 04C

Figure 5-4-2 Sample 04C

Figure 5-4-3 Sample 04D

Figure 5-4-4 Sample 04D

Figure 5-4-5 Sample 05C
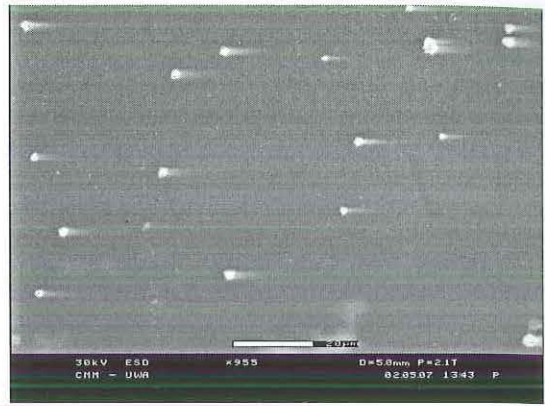
Figure 5-4-6 Sample 05C
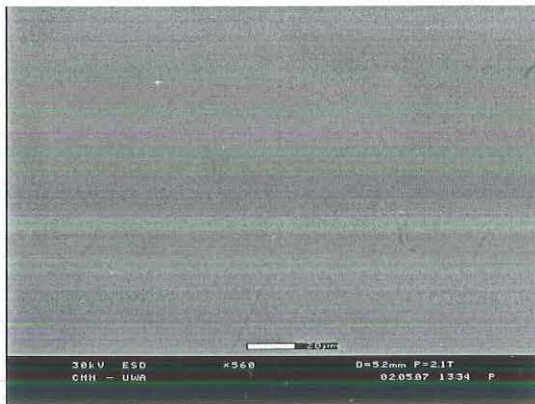
Figure 5-4-7 Sample 05D
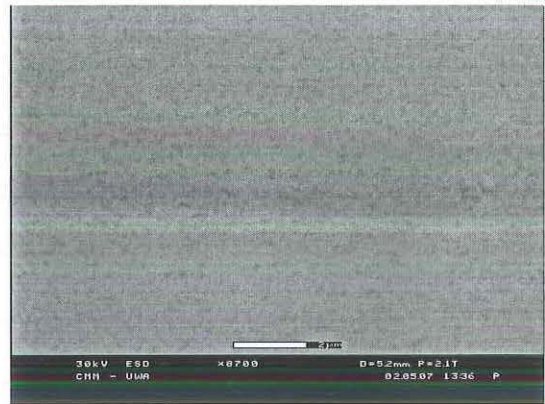
Figure 5-4-8 Sample 05D

Figure 5-4-9 Sample 06C
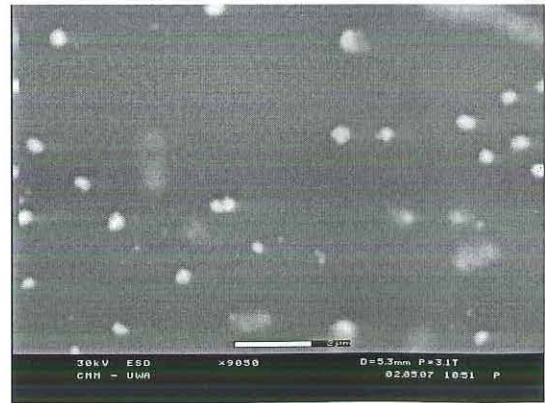
Figure 5-4-10 Sample 06C

Figure 5-4-11 Sample 06D
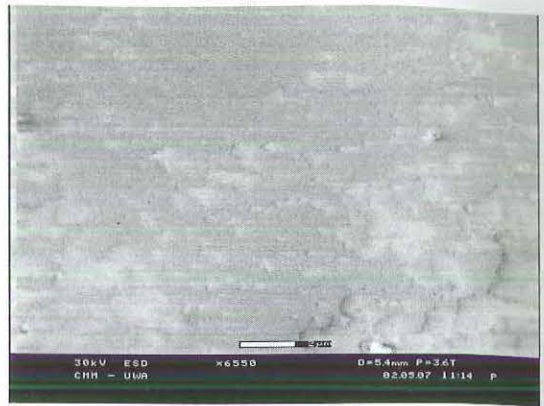
Figure 5-4-12 Sample 06D
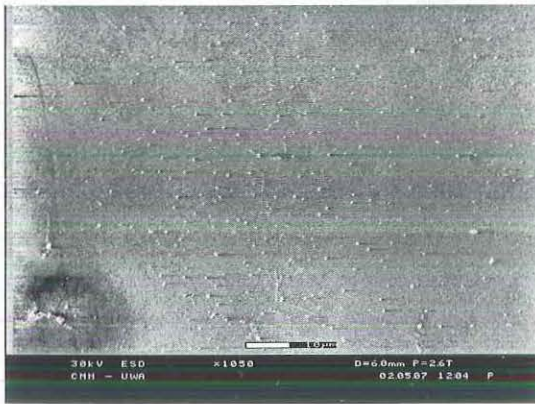
Figure 5-4-13 Sample 07C
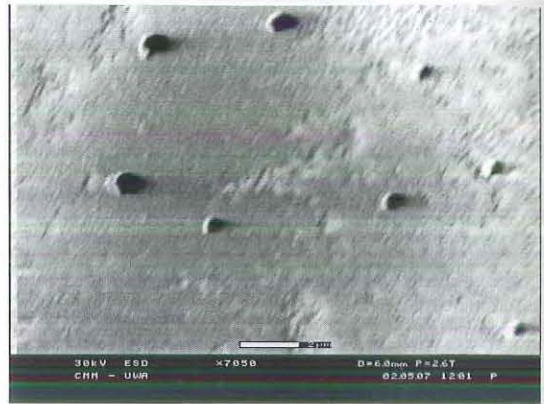
Figure 5-4-14 Sample 07C
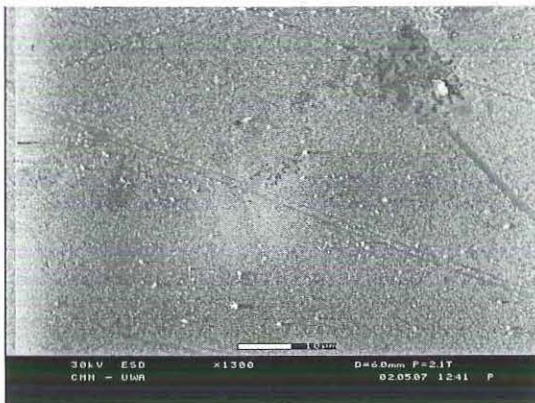
Figure 5-4-15 Sample 07D

Figure 5-4-16 Sample 07D

Figure 5-4-17 Sample 08C
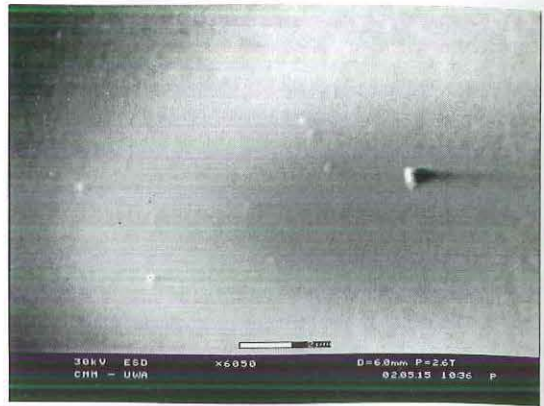
Figure 5-4-18 Sample 08C

Figure 5-4-19 Sample 08D
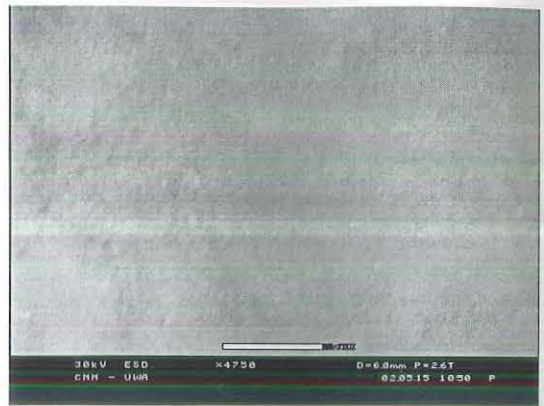
Figure 5-4-20 Sample 08D

Figure 5-4-21 Sample 09C

Figure 5-4-22 Sample 09C
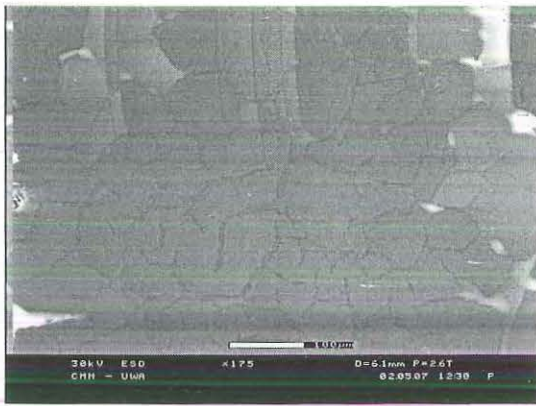
Figure 5-4-23 Sample 09D
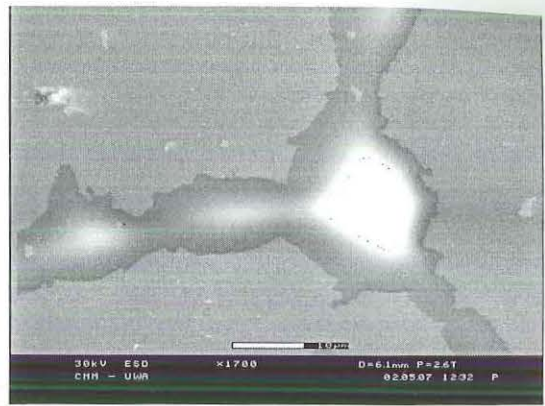
Figure 5-4-24 Sample 09D

Figure 5-4-25 Sample 10C

Figure 5-4-26 Sample 10C

Figure 5-4-27 Sample 10D

Figure 5-4-28 Sample 10D

Figure 5-4-29 Sample 11C

Figure 5-4-30 Sample 11C

Figure 5-4-31 Sample 11D

Figure 5-4-32 Sample 11D

Figure 5-4-33 Sample 12C

Figure 5-4-34 Sample 12C

Figure 5-4-35 Sample 12D

Figure 5-4-36 Sample 12D

Figure 5-4-37 Sample 14C

Figure 5-4-38 Sample 14C

Figure 5-4-39 Sample 14D

Figure 5-4-40 Sample 14D
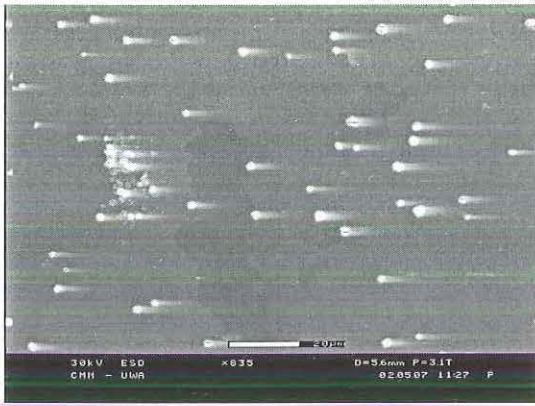
Figure 5-4-41 Sample 15C

Figure 5-4-42 Sample 15C
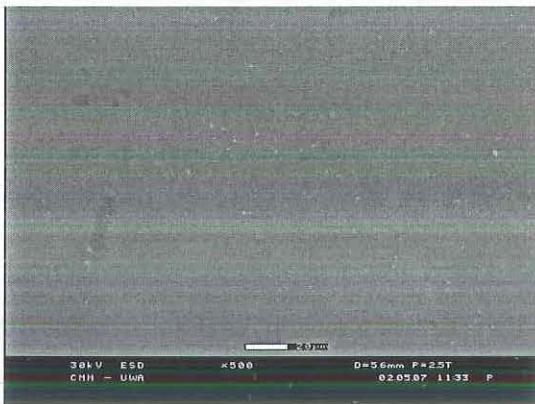
Figure 5-4-43 Sample 15D
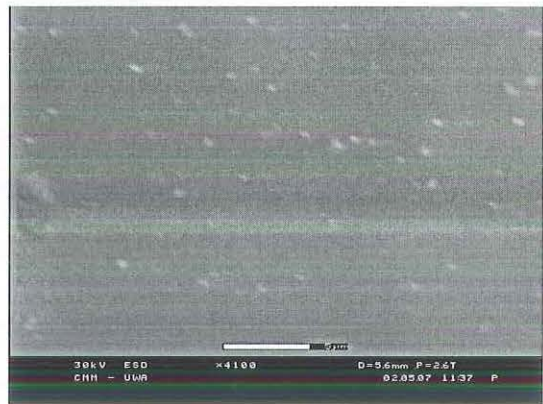
Figure 5-4-44 Sample 15D

5-5 Atomic Force Microscopy

The AFM data was arranged in raw data files. To analysis these data files the Digital Instruments offline AFM software was required. When analysed with the offline software the data is represented as two images, the left image is a height profile of the point of the surface being examined. The right image is a difference map of the first image. Also, below the images is a summary of the examination conditions, most importantly the size of the image is shown here. Two images are shown for each of the samples that were examined, they are in Figures 5-5-1 through to 5-5-24. The first pair of images is of a relatively wide area of 50μm, the second is a close up at 5μm. A second set of images is also given in Figures 5-5-25 through to 5-5-36. These images are a three dimensional plot of the 5μm images presented. They give a clear indication of the vertical distribution of the films surface features. The three dimensional images were constructed by manipulating the data with the offline analysis software.

When inspecting the images produced by the AFM one important aspect that recurs throughout the data is the presence of nodule like structures at the surface of the annealed films. This can be seen very clearly in sample 04B in Figures 5-5-1 and 5-5-2. The nodules appear to be approximately 1μm in diameter, and using Figure 5-5-25, they are a little over 200nm high. These nodule like structures do not appear on the as-deposited films. This would suggest that the nodules develop during the annealing post deposition process of the production of the samples. A comparison of the as-deposited films in Figures 5-5-1, 5-5-2 and the annealed films in Figures 5-5-3 5-5-4 clearly shows the absence of the nodule structures in the as-deposited films. This data is in agreement with that present by the CCI measurements.

Another effect of the annealing process is the increase in roughness of the grain like surface of the CdS thin films. A comparison of the as-deposited and annealed samples in Figures 5-5-31, 5-5-32, 5-5-35, and 5-5-36 clearly shows this increase in roughness. One other feature that presents itself in all the images is horizontal lines. These are not actually present on the samples but are in fact a product of the microscope tip dragging across the surface and scoring the samples, when the very point of the tip bends due to normal use it can work to produce these lines as well. This can be seen very clearly in Figure 5-5-11, where the effect is quite severe. The lines also present themselves in Figures 5-5-14, and 5-5-21 but to a much less severe degree.
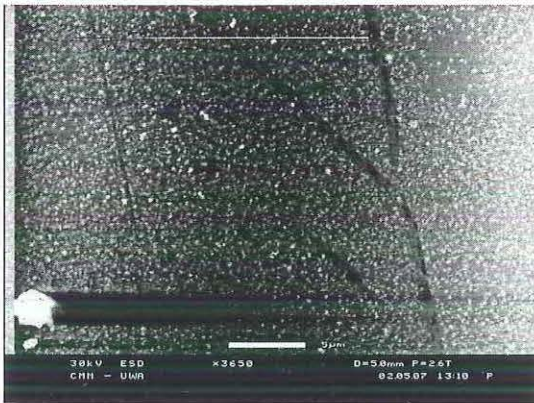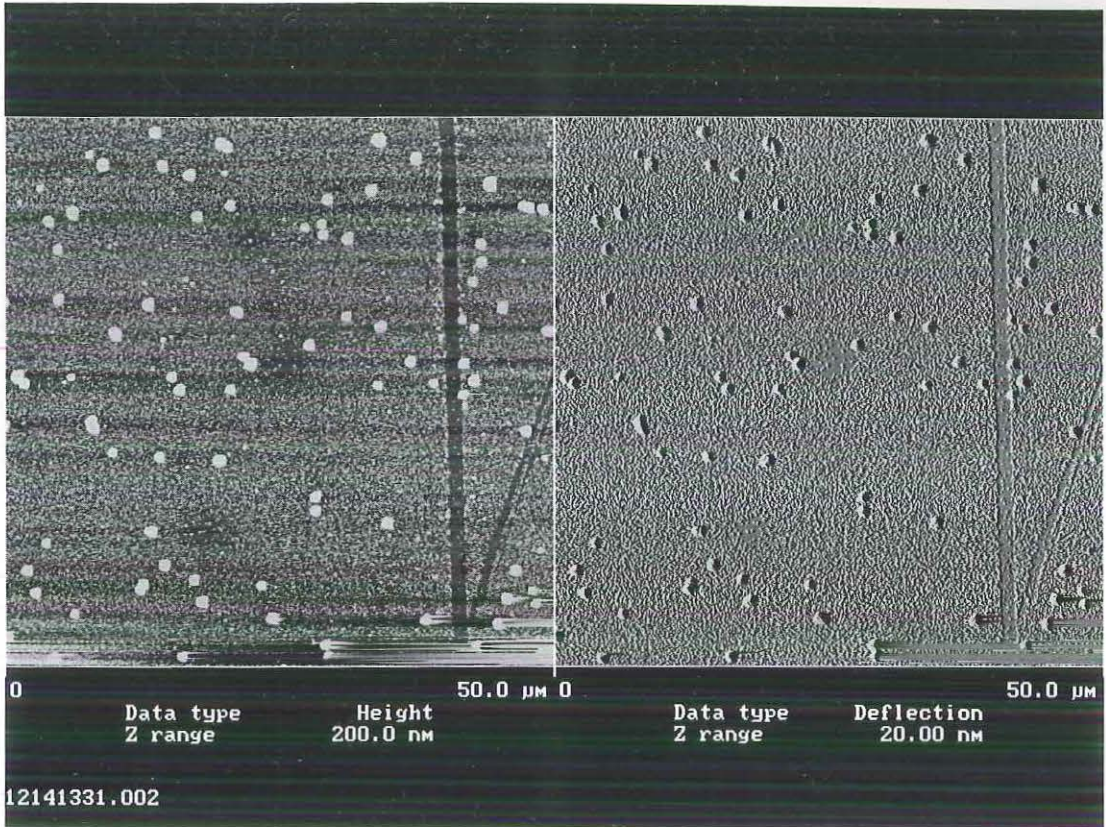
Figure 5-5-1 Sample 04B
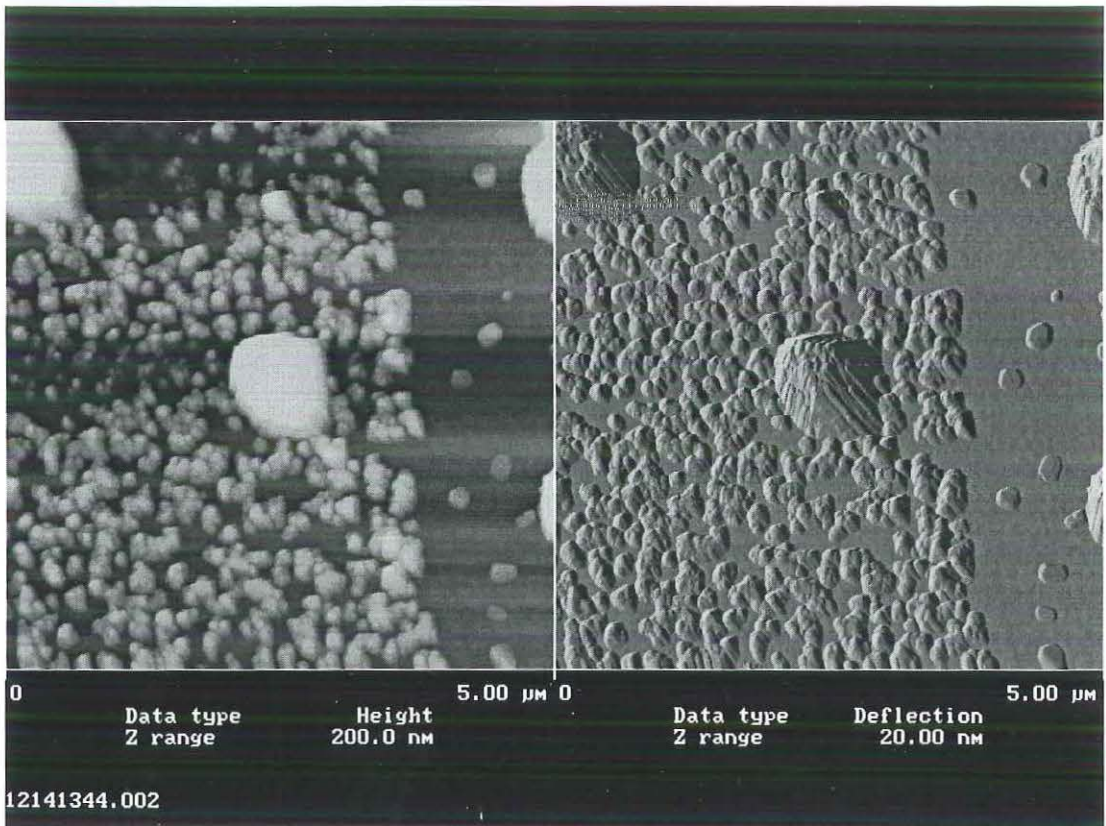
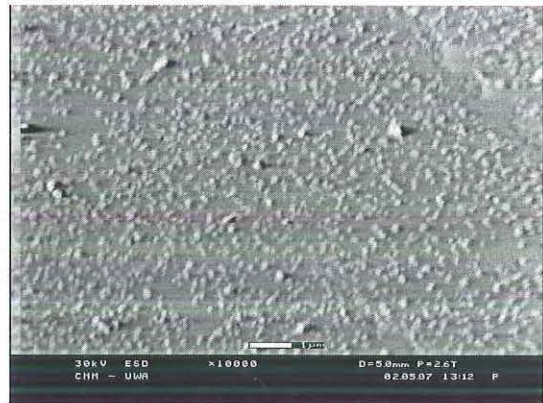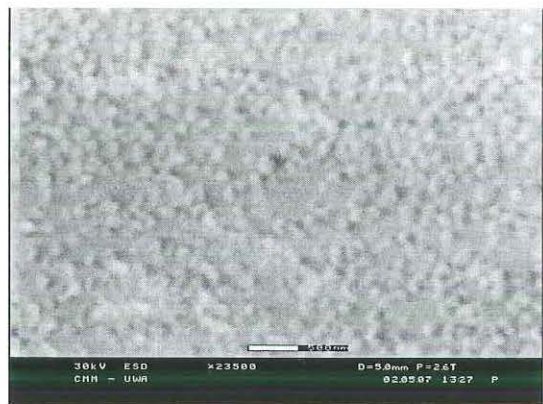Figure 5-5-2 Sample 04B
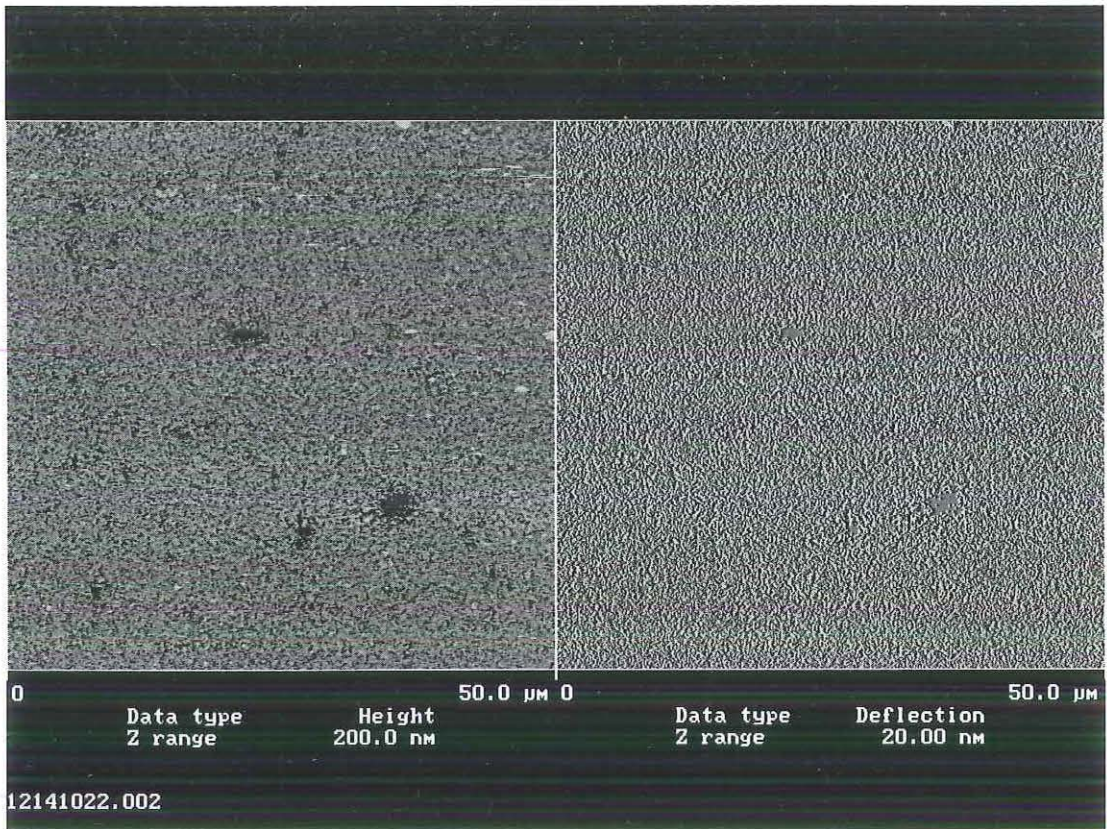
Figure 5-5-3 Sample 04E
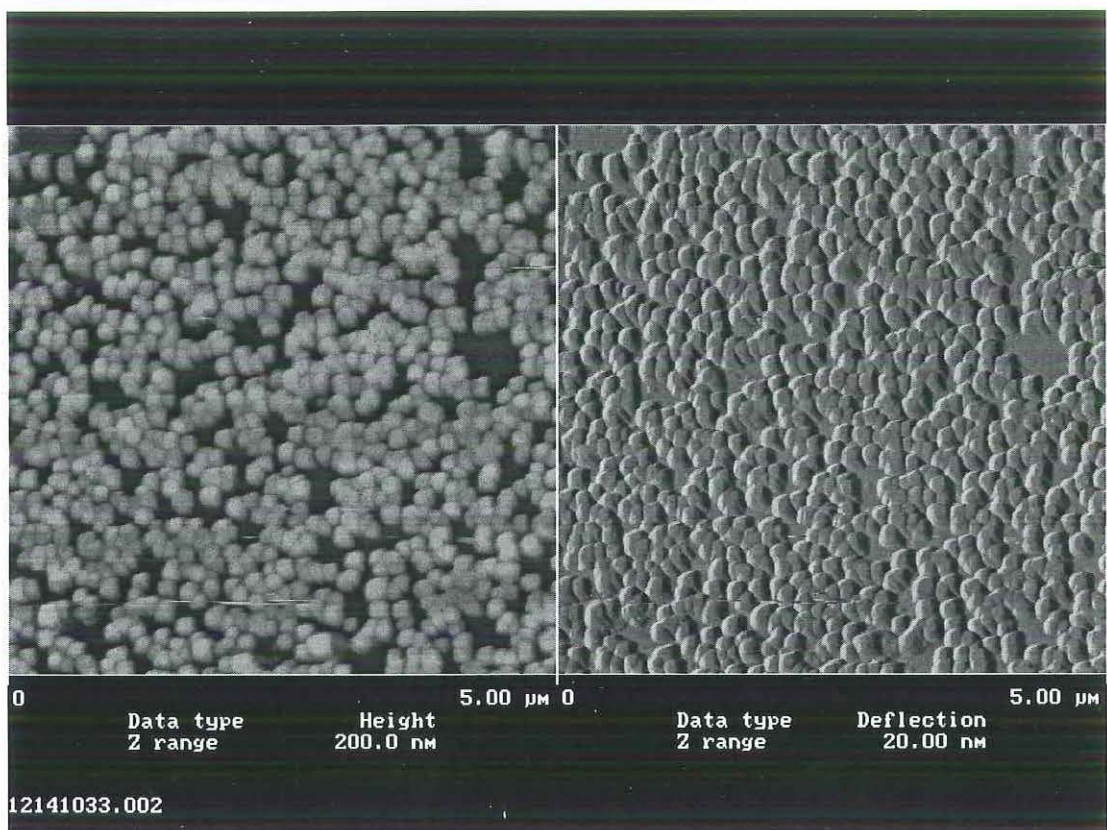
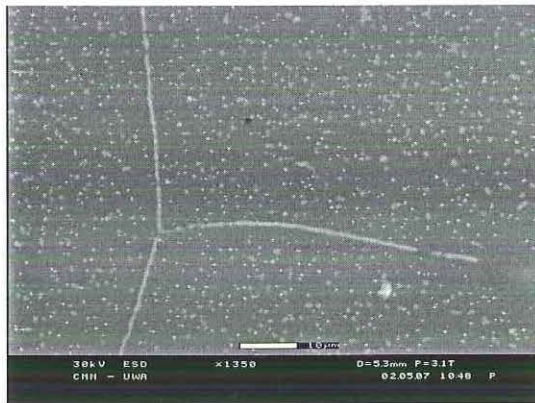Figure 5-5-4 Sample 04E
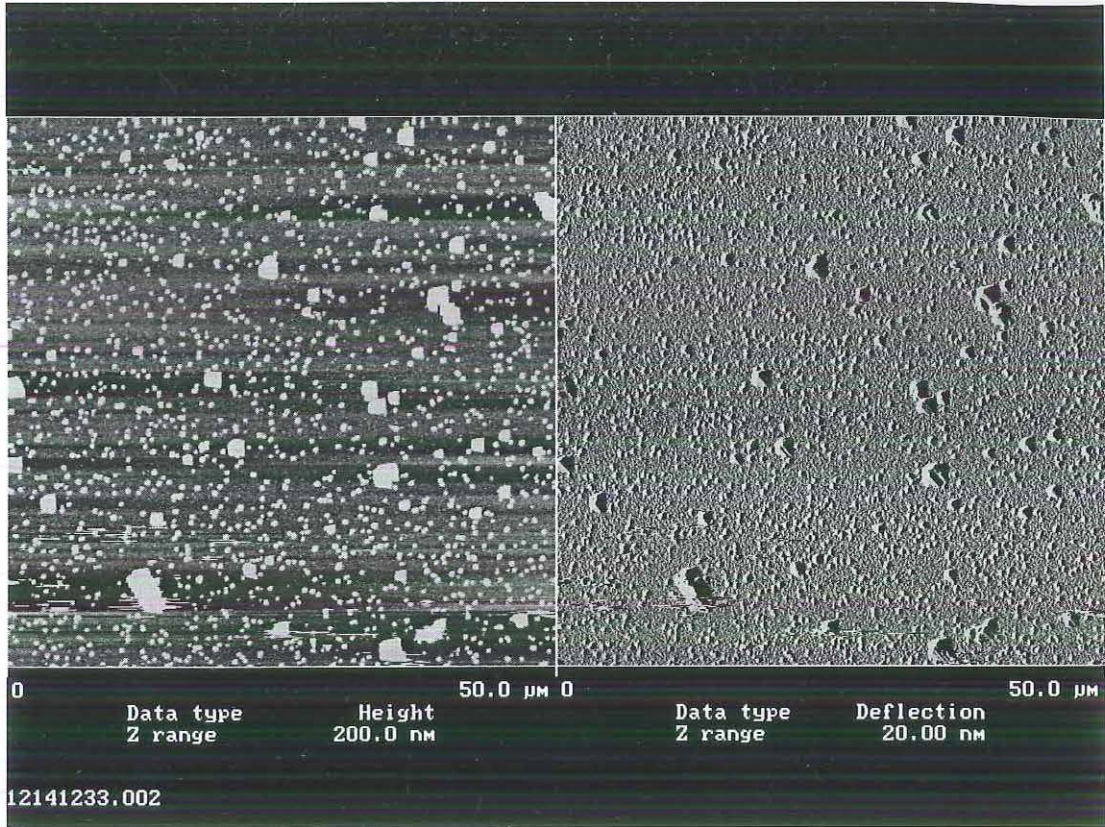
Figure 5-5-5 Sample 05B

Figure 5-5-6 Sample 05B

Data type   Height
Z range   200.0 nм

Data type   Deflection
Z range   20.00 nм

0   50.0 µм 0   50.0 µм

12141047.002

Figure 5-5-7 Sample 05E

Data type   Height
Z range   200.0 nм

Data type   Deflection
Z range   20.00 nм

0   4.94 µм 0   4.94 µм

12141100.002
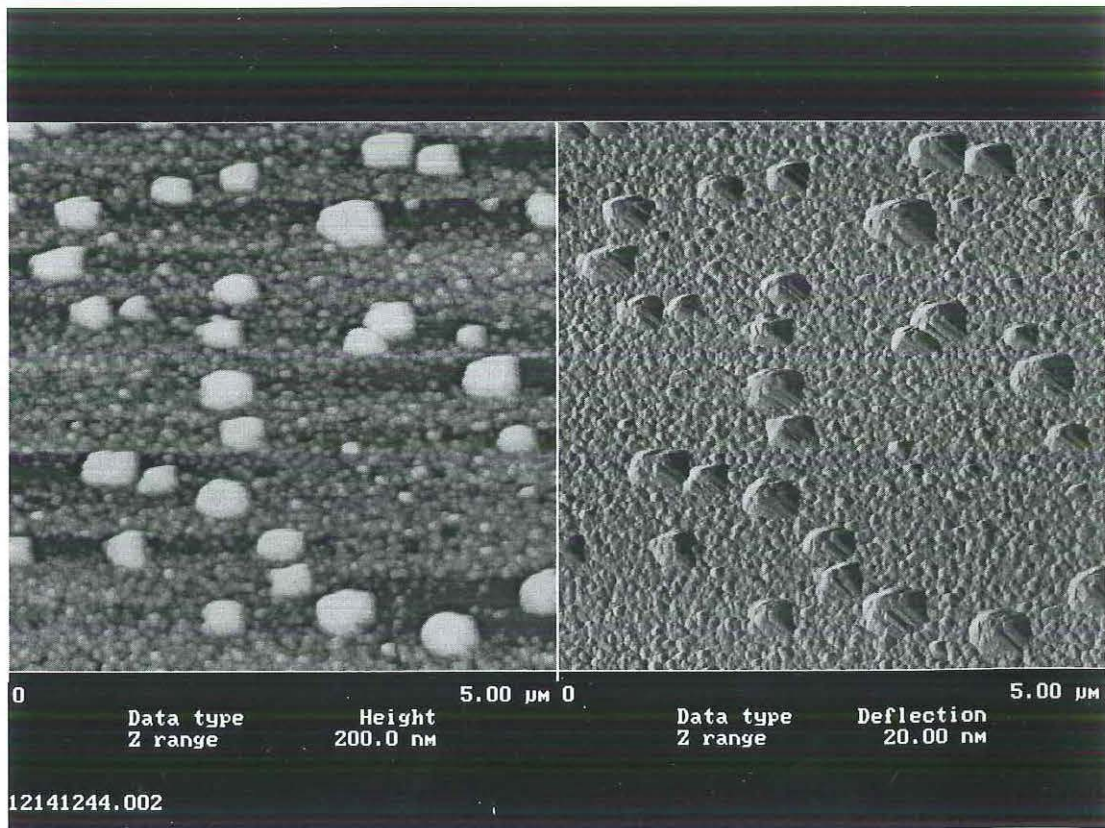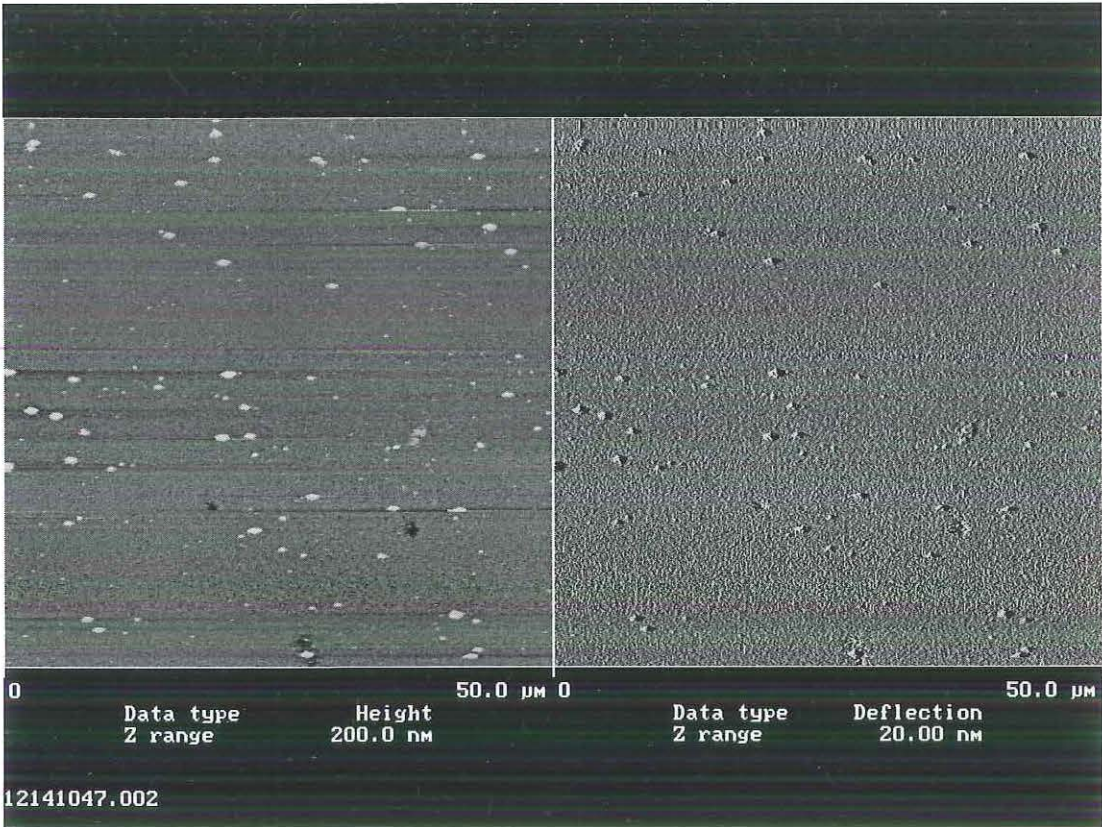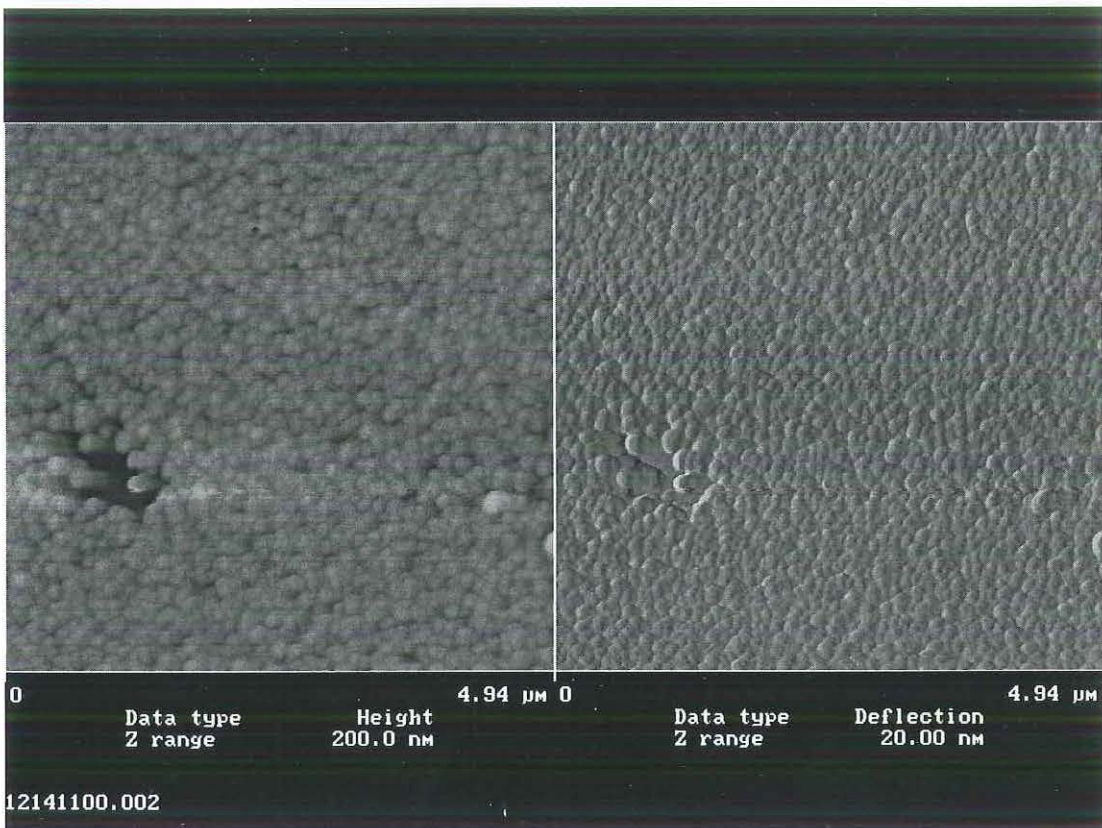
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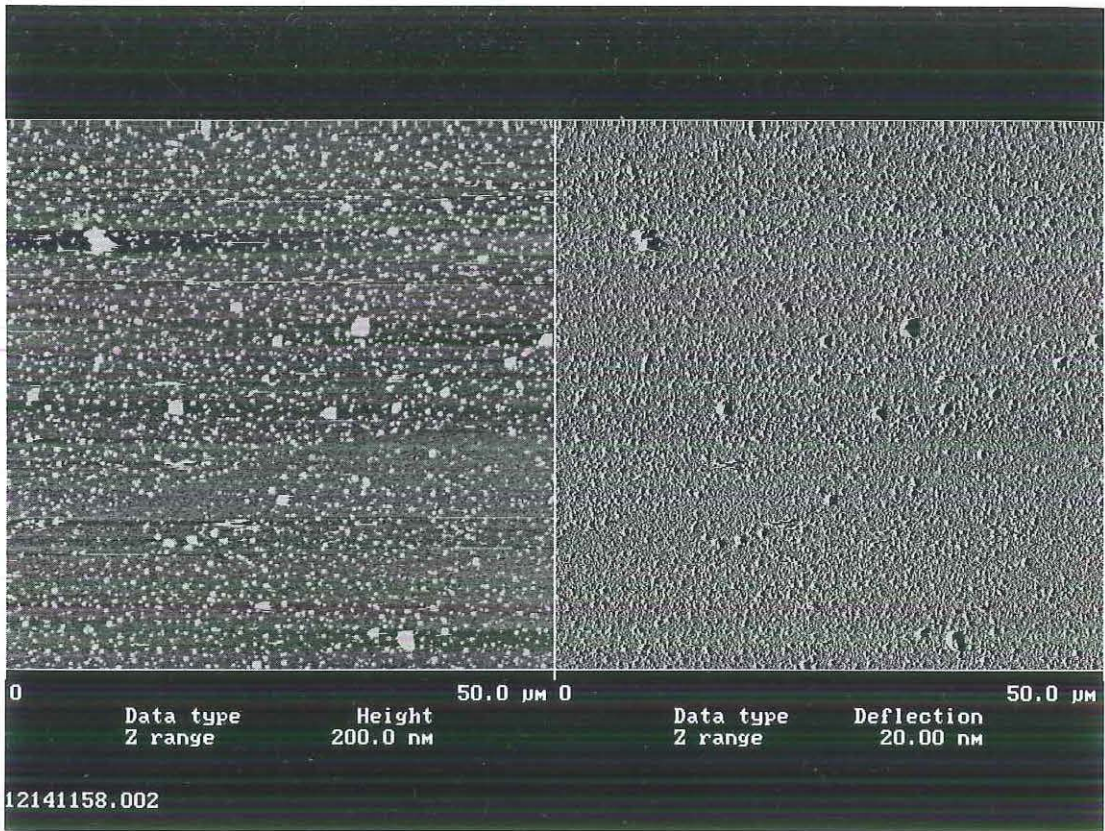
Figure 5-5-9 Sample 08B

Figure 5-5-10 Sample 08B

0   50.0 µM 0   50.0 µM

Data type	Height	Data type	Deflection
Z range	200.0 nm	Z range	20.00 nm

12141130.002

Figure 5-5-11 Sample 08E

0   5.00 µM 0   5.00 µM

Data type	Height	Data type	Deflection
Z range	200.0 nm	Z range	20.00 nm

12141141.002
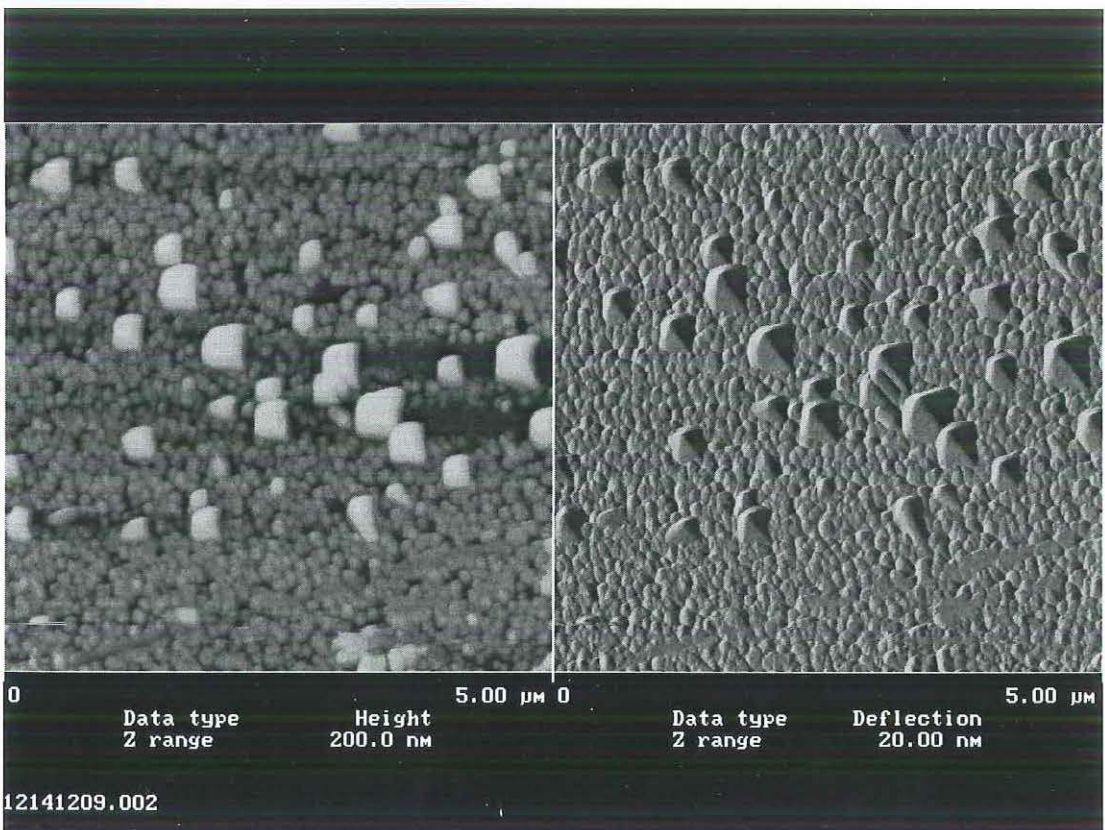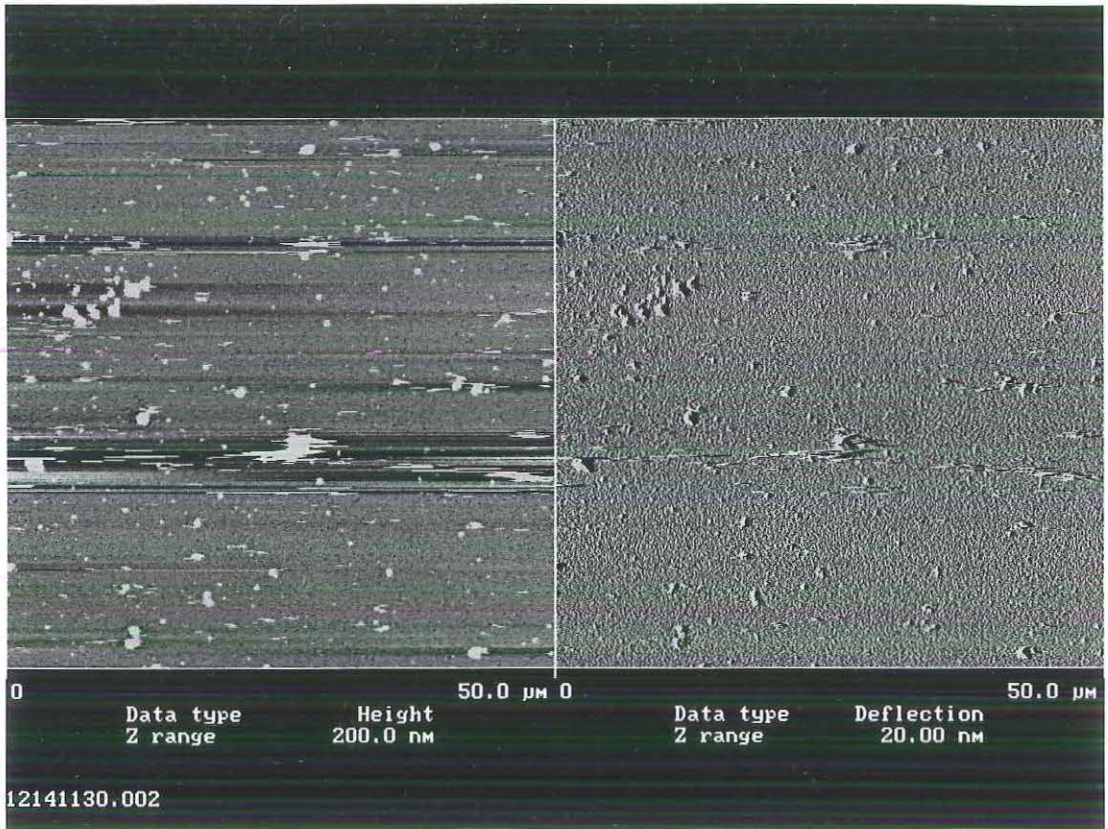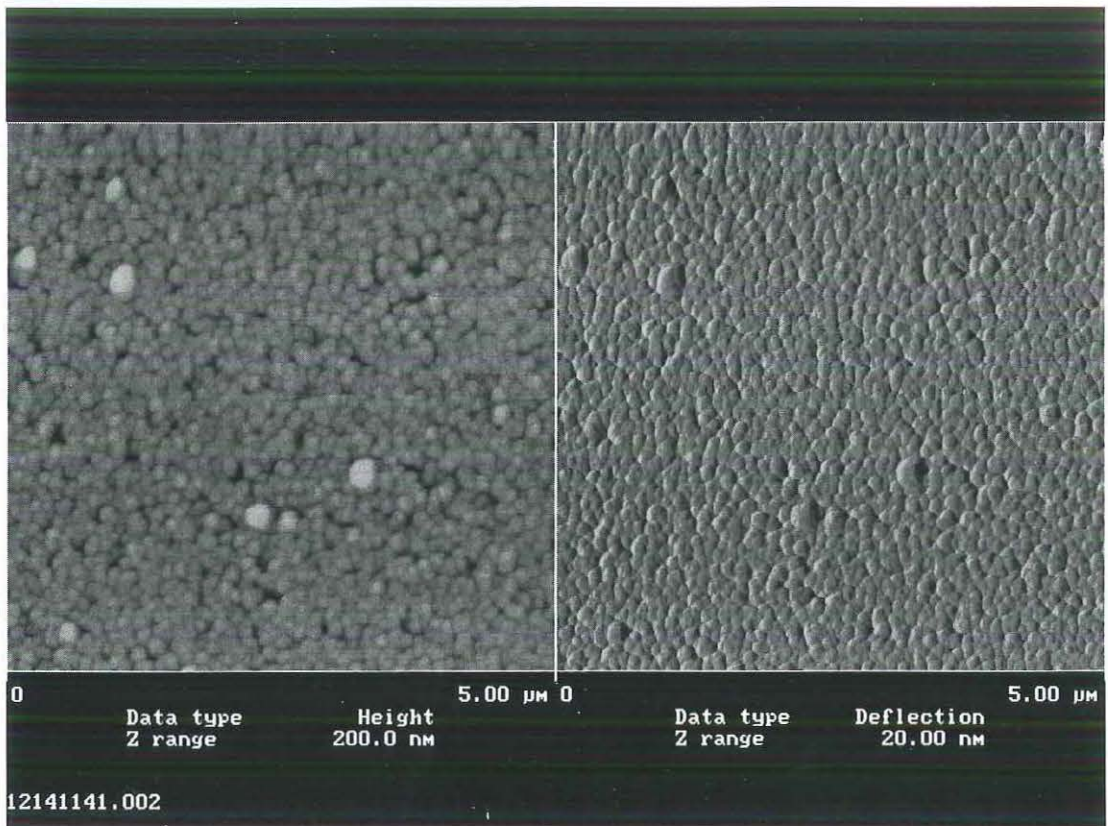
Figure 5-5-12 Sample 08E
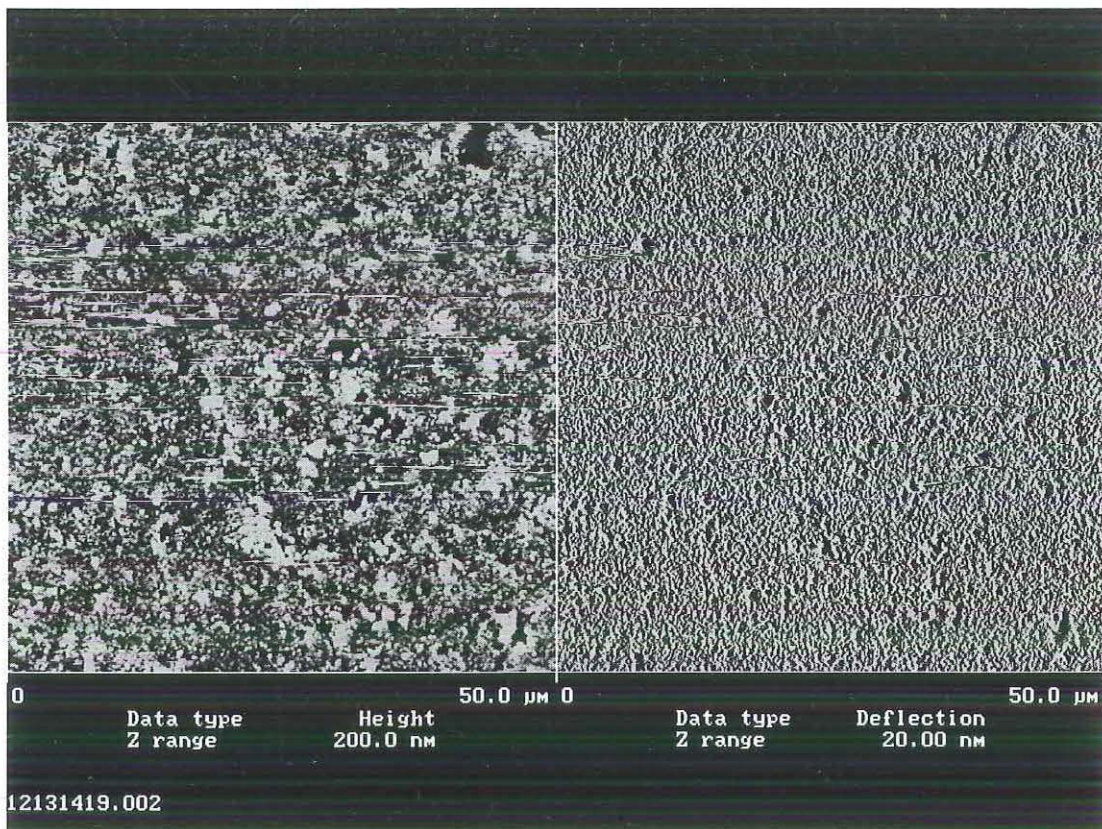
Figure 5-5-13 Sample 11B
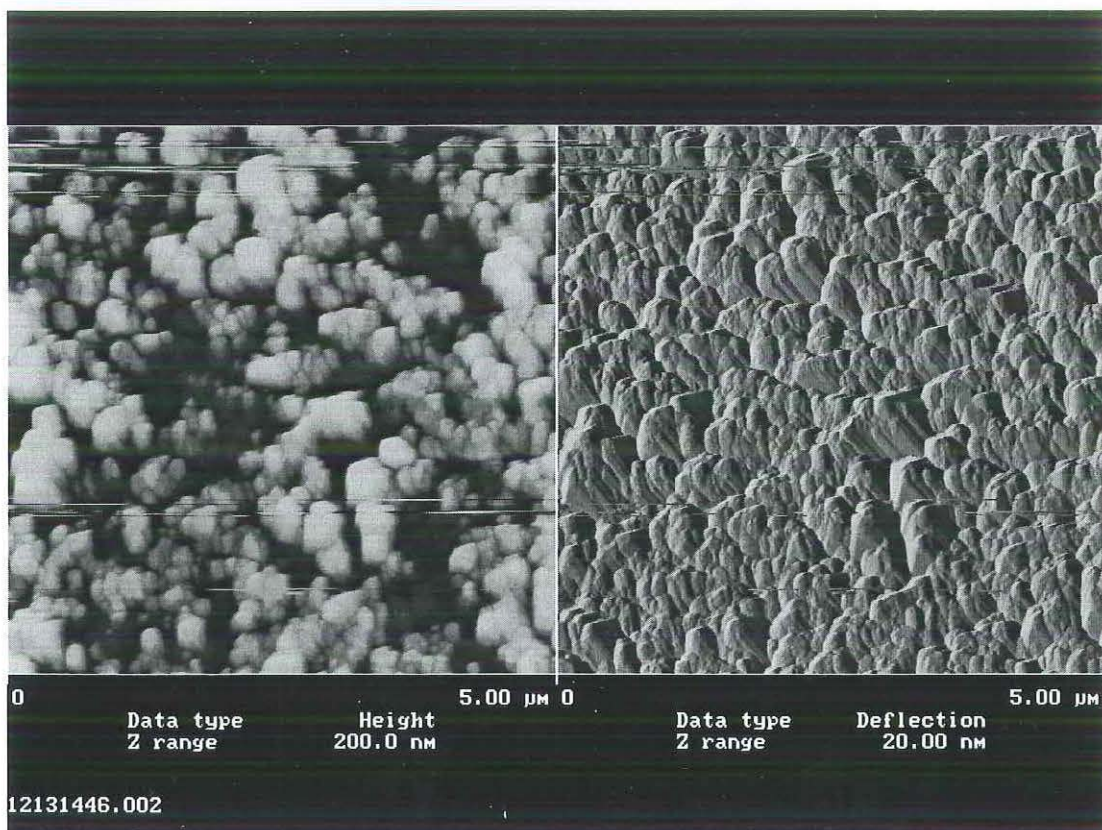
Figure 5-5-14 Sample 11B

74
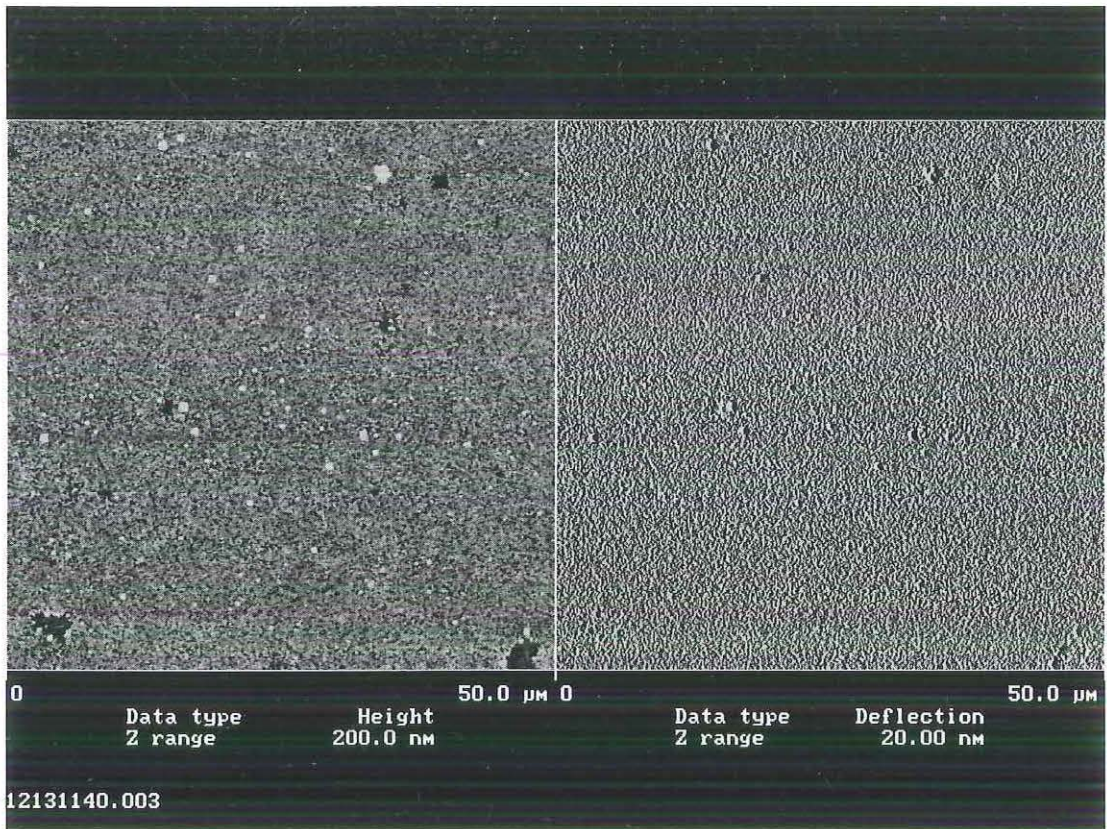
Figure 5-5-15 Sample 11E
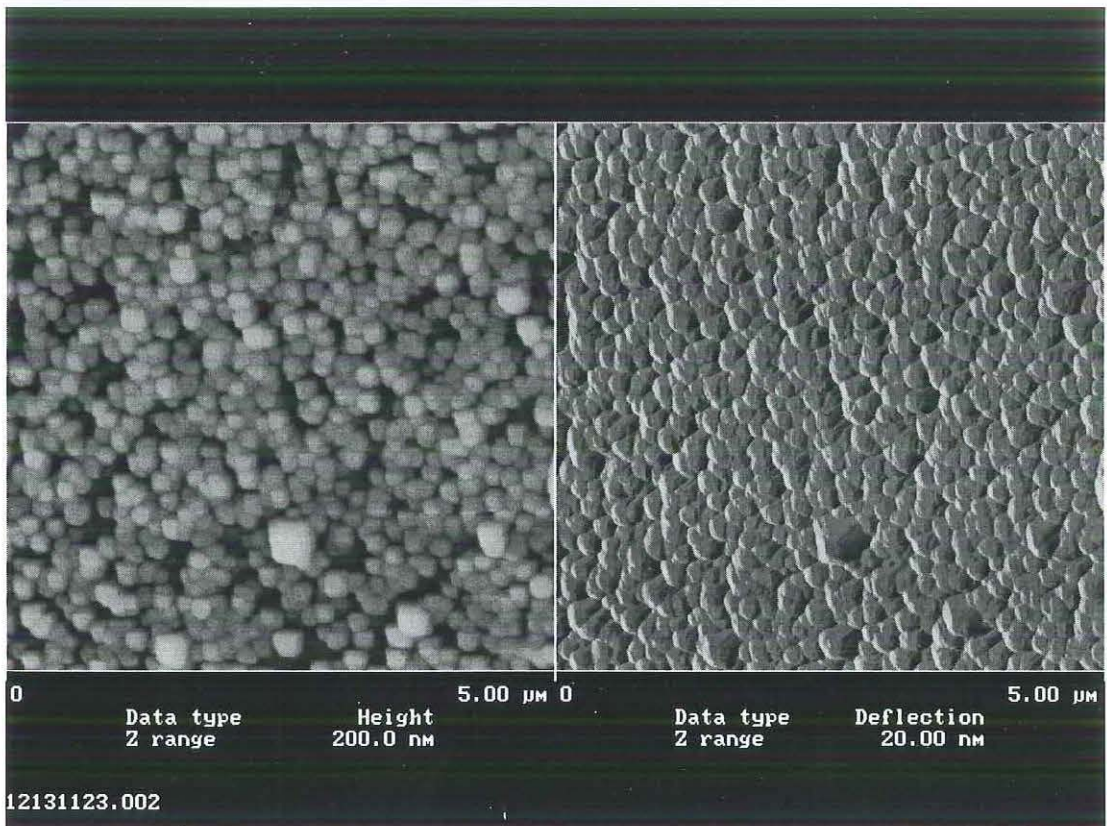
Figure 5-5-16 Sample 11E
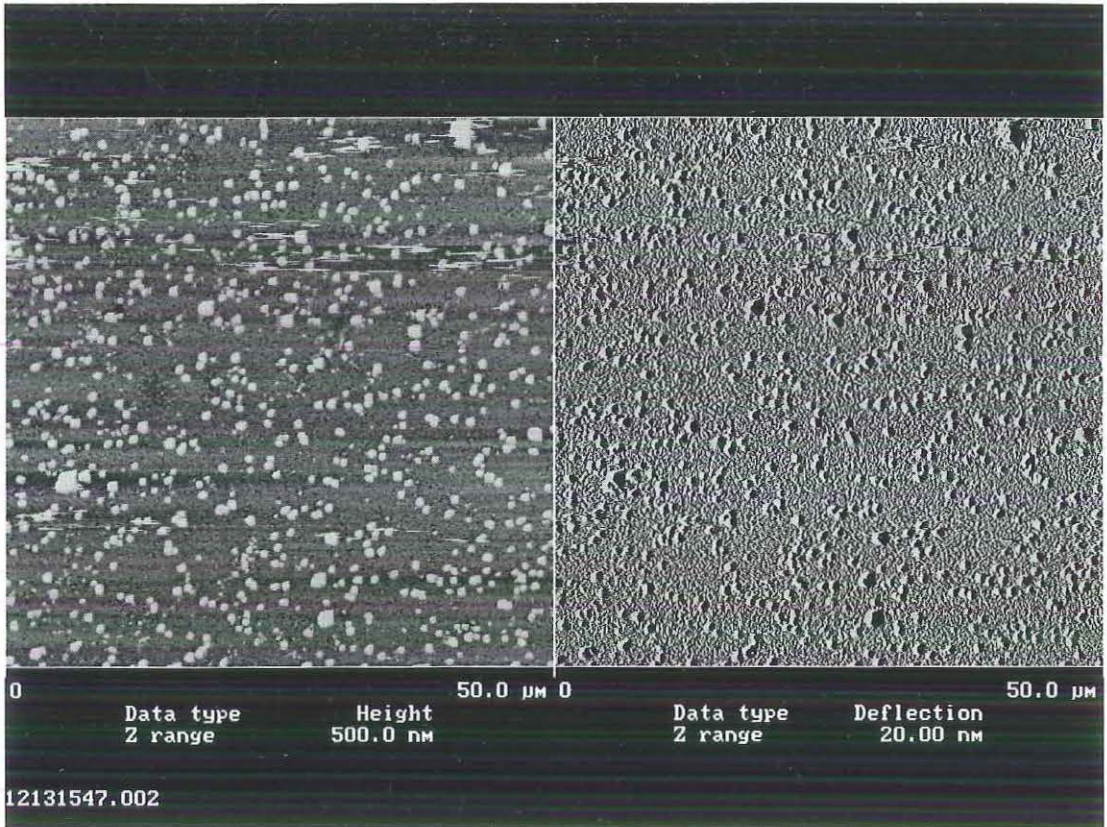
Figure 5-5-17 Sample 14B

Figure 5-5-18 Sample 14B

0   50.0 μM 0   50.0 μM

Data type   Height   Data type   Deflection
Z range   200.0 nM   Z range   20.00 nM

12131638.002

Figure 5-5-19 Sample 14E

0   5.00 μM 0   5.00 μM

Data type   Height   Data type   Deflection
Z range   200.0 nM   Z range   20.00 nM

12131650.002
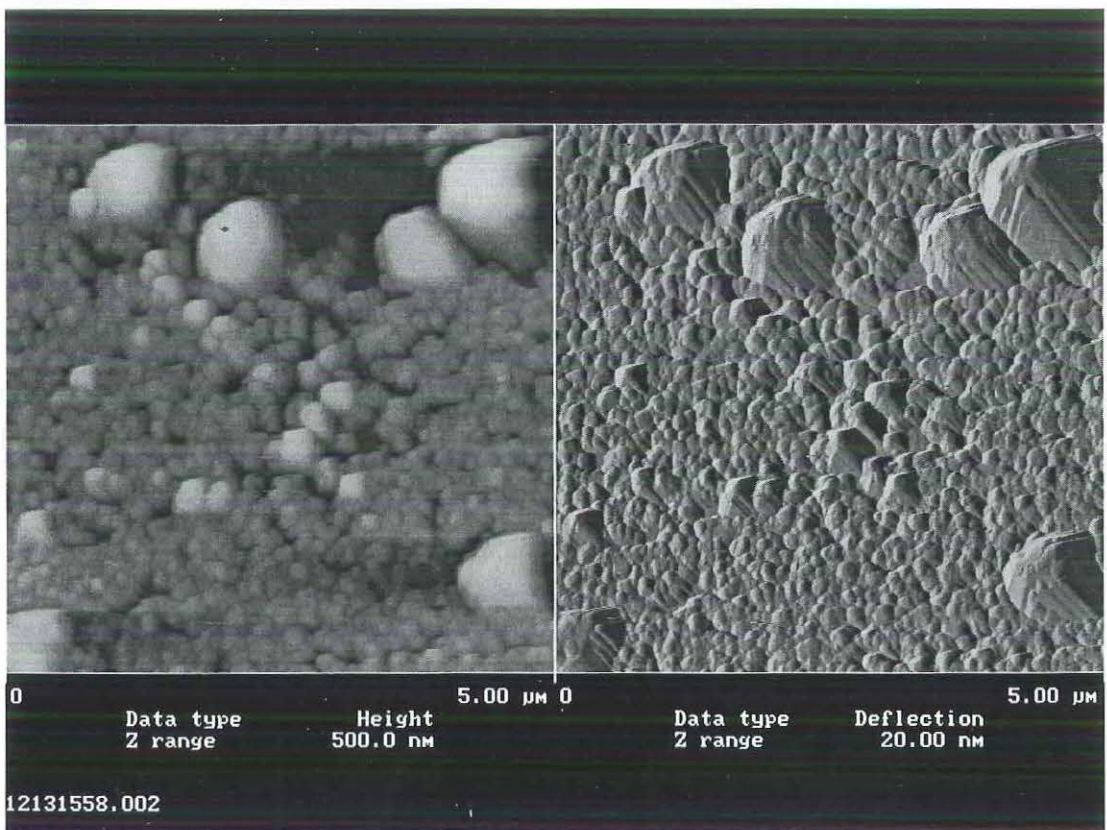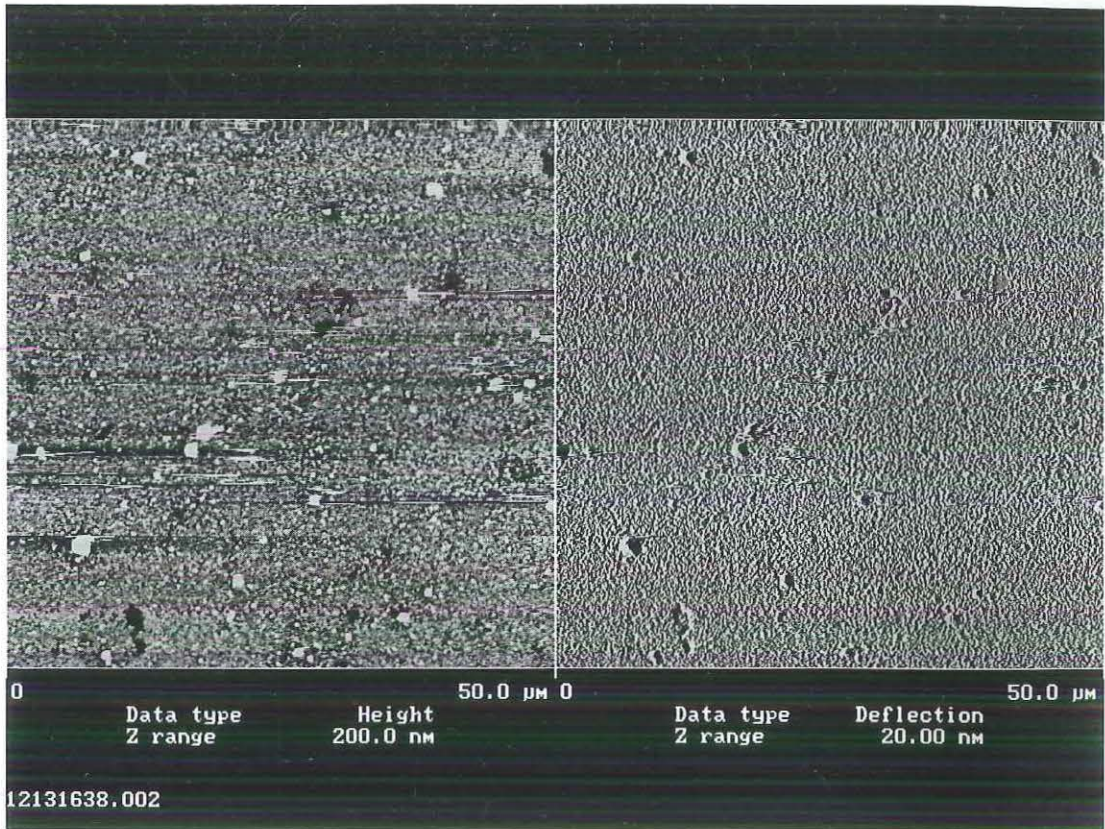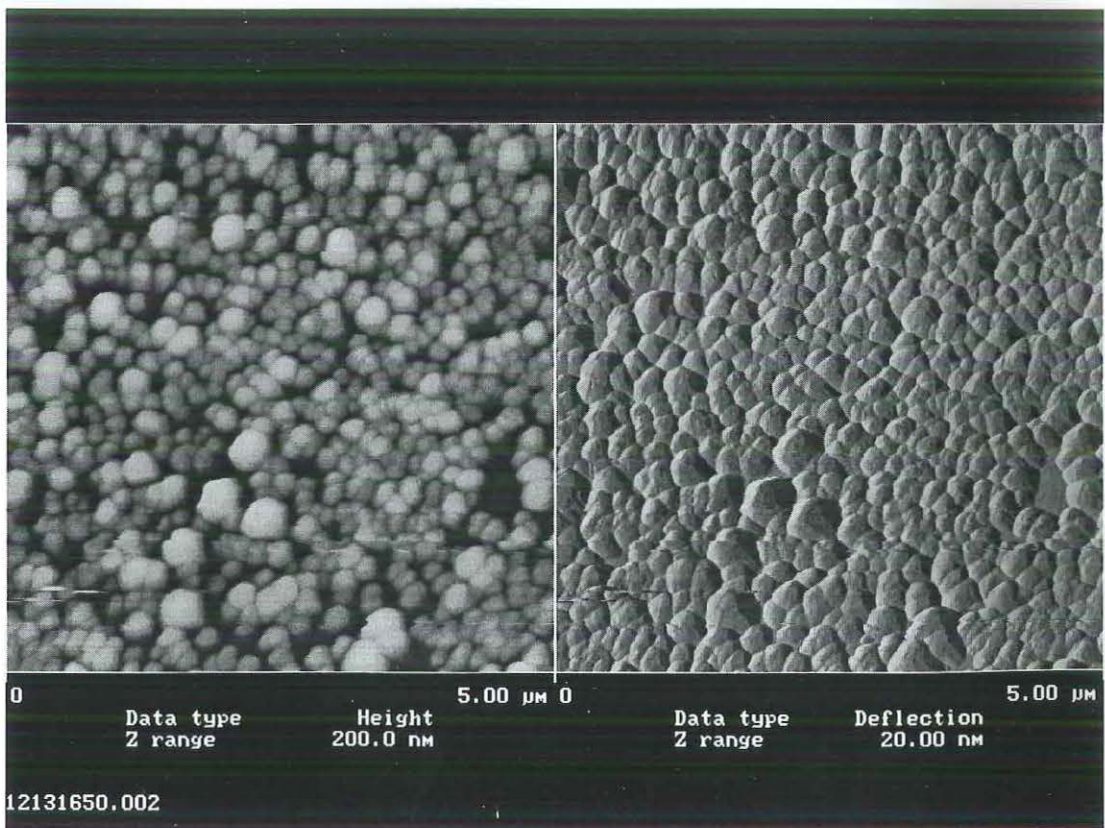
Figure 5-5-20 Sample 14E
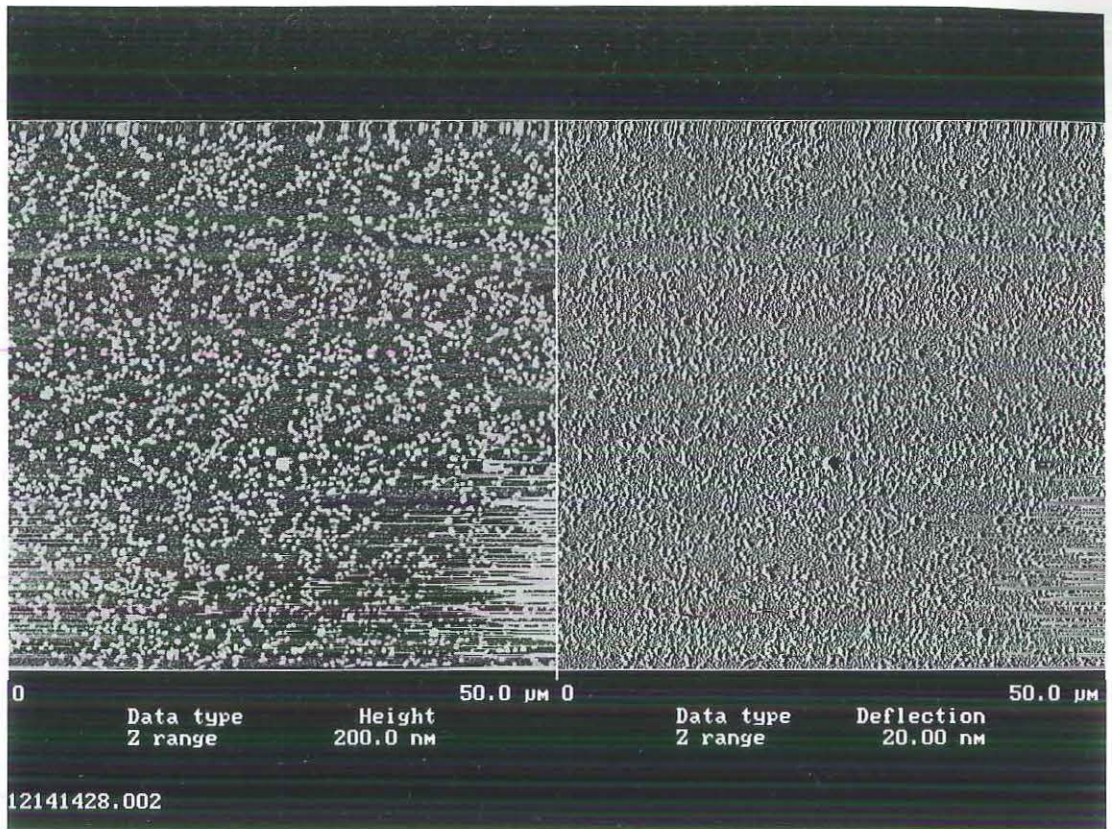
Figure 5-5-21 Sample 15B
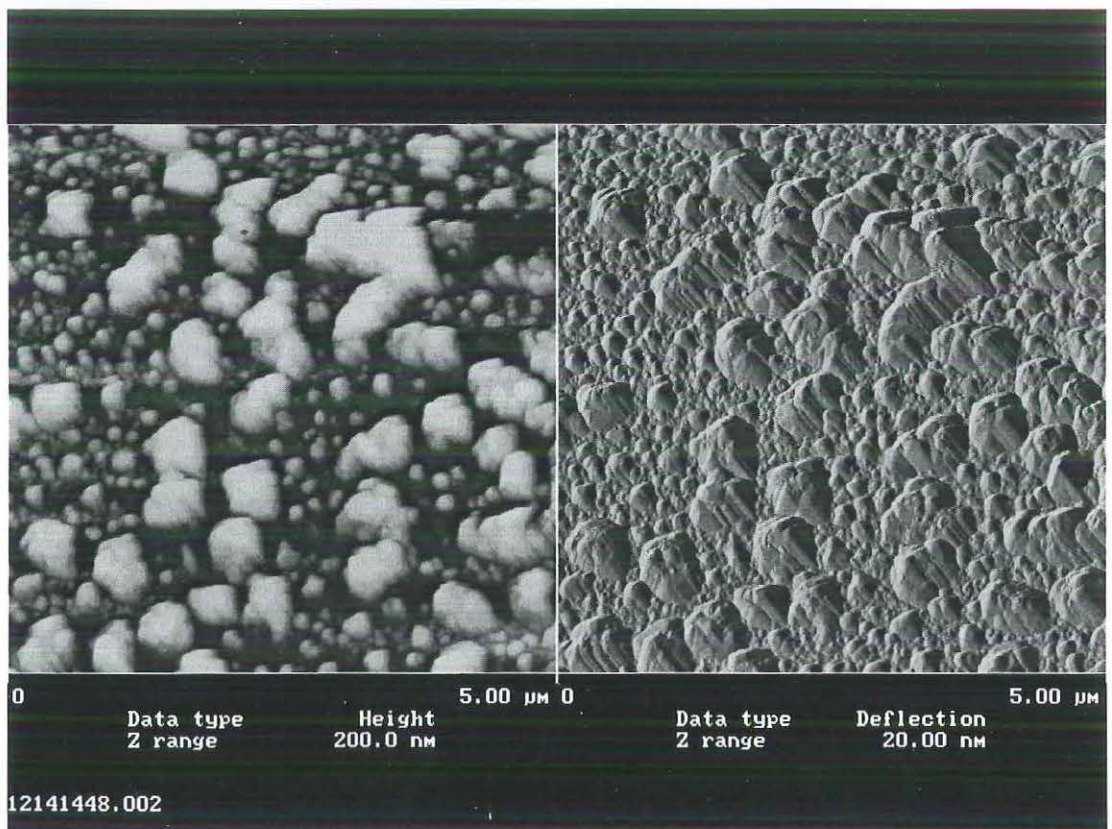
Figure 5-5-22 Sample 15B

Figure 5-5-23 Sample 15E

Data type	Height
Z range	200.0 nm

0   50.0 μm

12141401.002

Data type	Deflection
Z range	20.00 nm

0   50.0 μm

Figure 5-5-24 Sample 15E

Data type	Height
Z range	200.0 nm

0   5.00 μm

12141414.002

Data type	Deflection
Z range	20.00 nm

0   5.00 μm
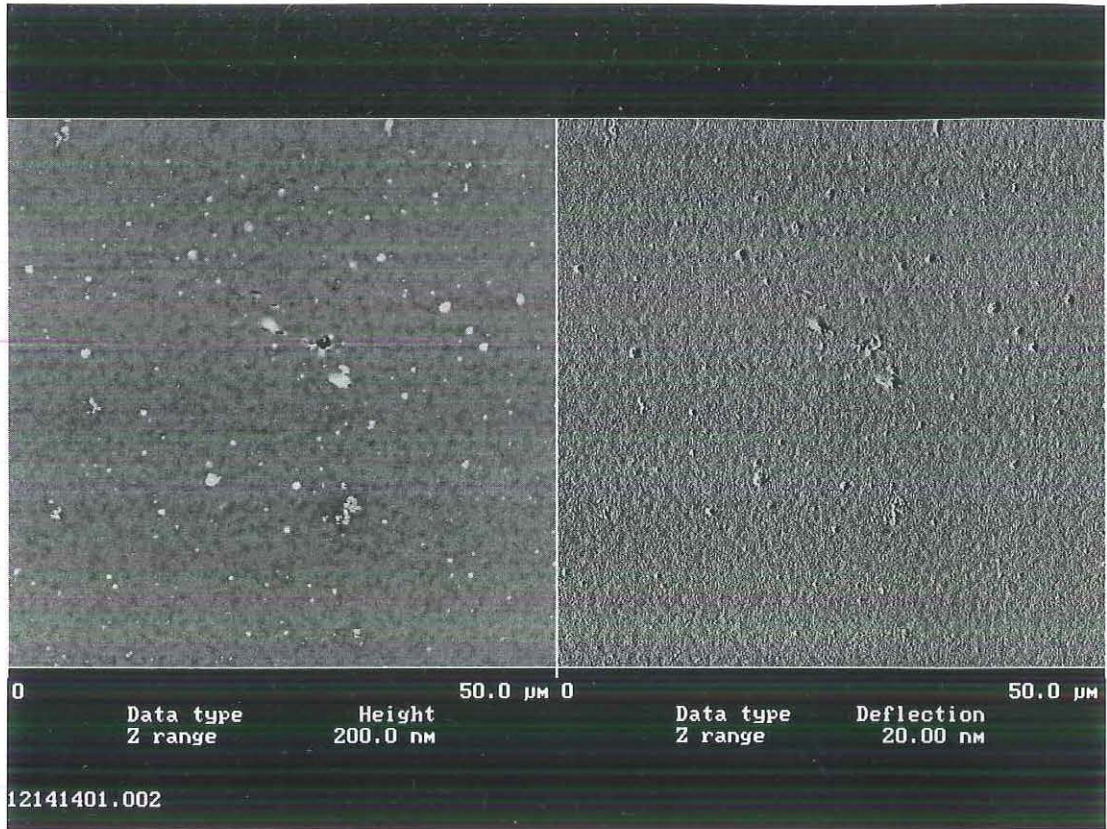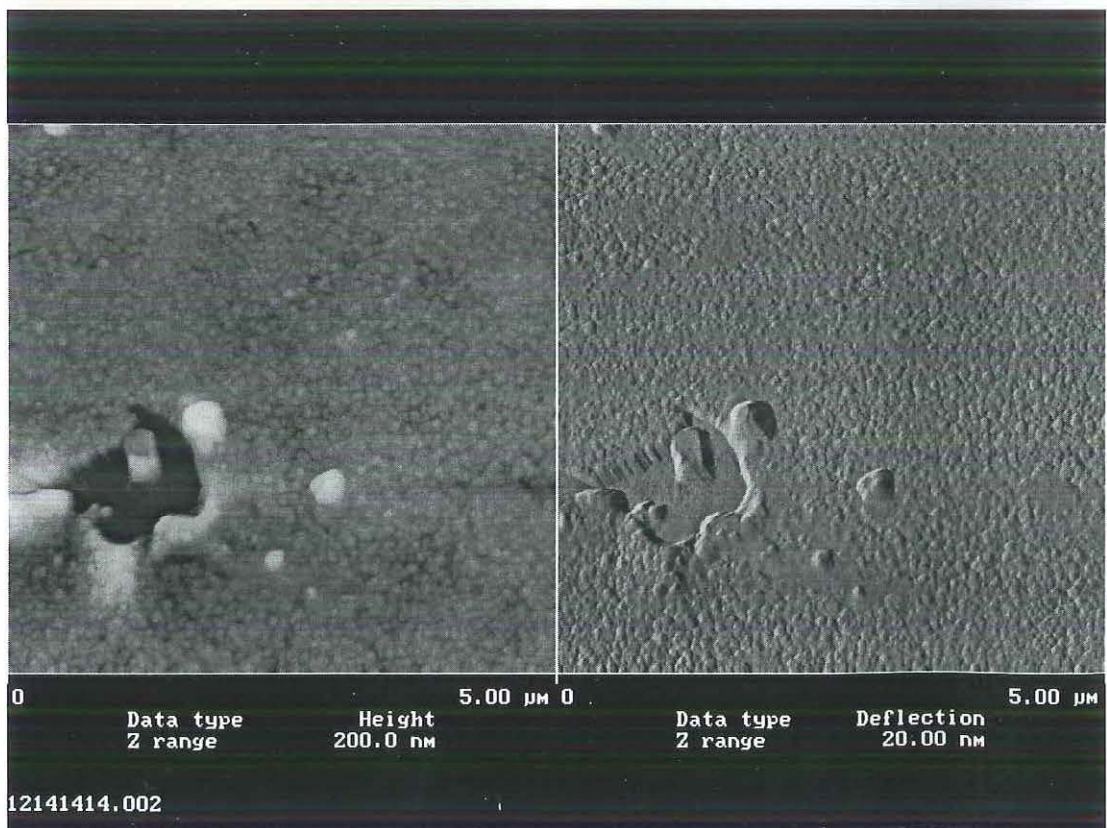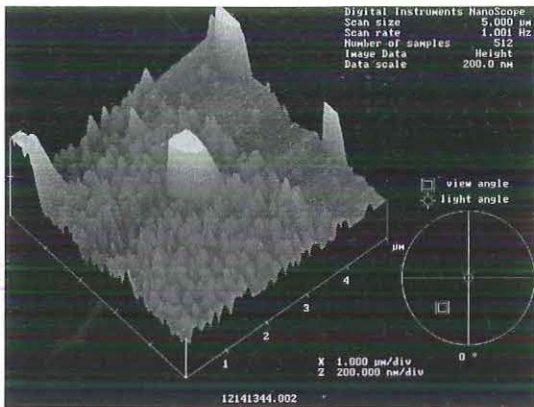
Figure 5-5-25 Sample 04B
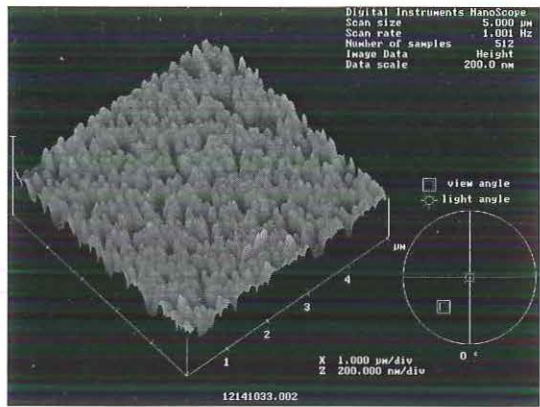
Figure 5-5-26 Sample 04E
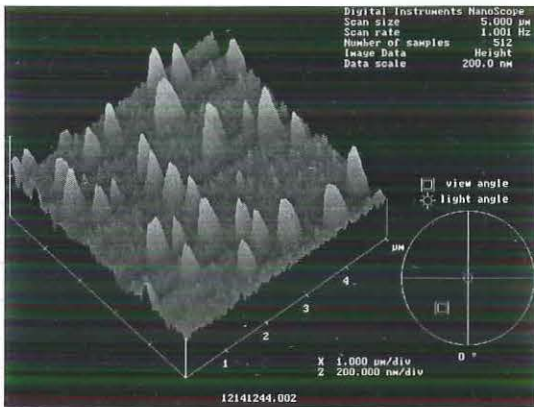
Figure 5-5-27 Sample 05B
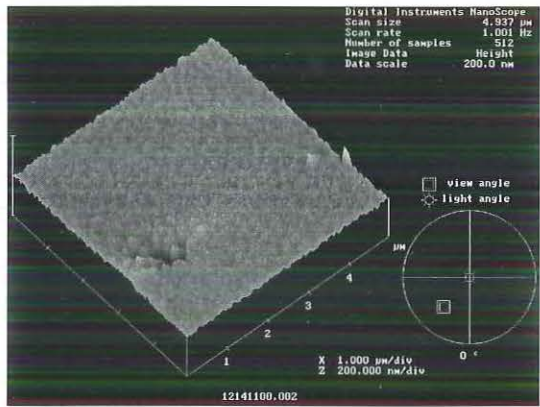
Figure 5-5-28 Sample 05E
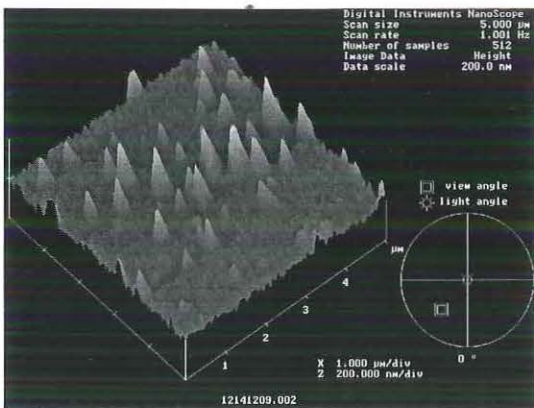
Figure 5-5-29 Sample 08B
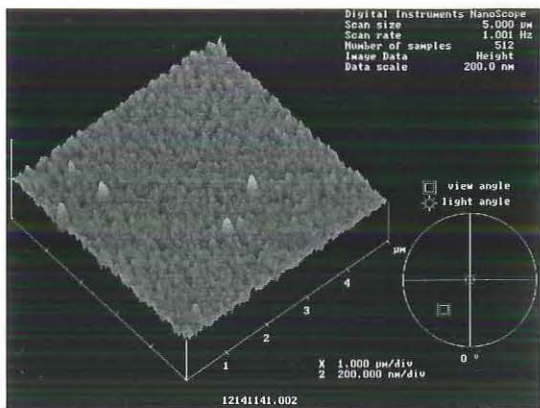
Figure 5-5-30 Sample 08E
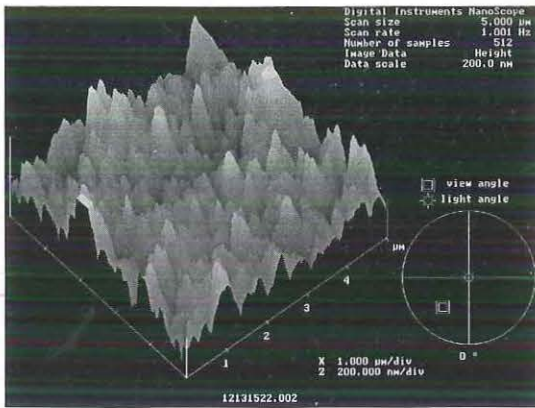
Figure 5-5-31 Sample 11B
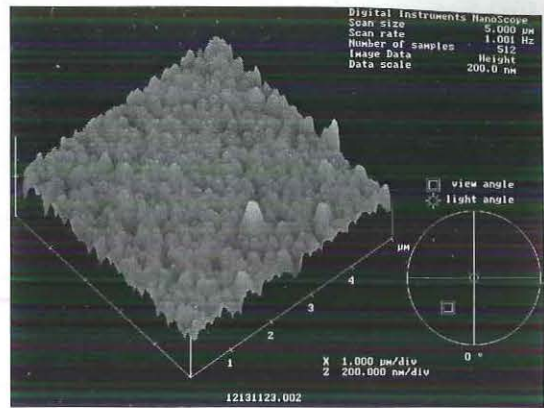
Figure 5-5-32 Sample 11E
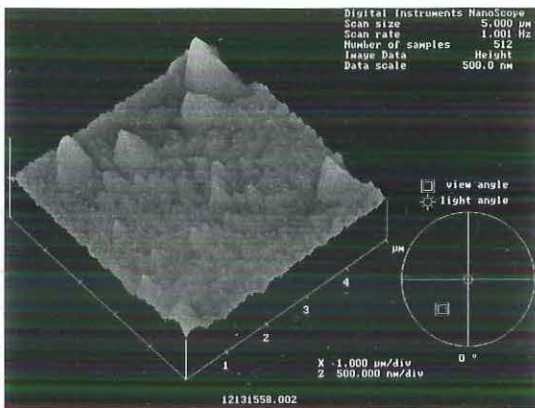
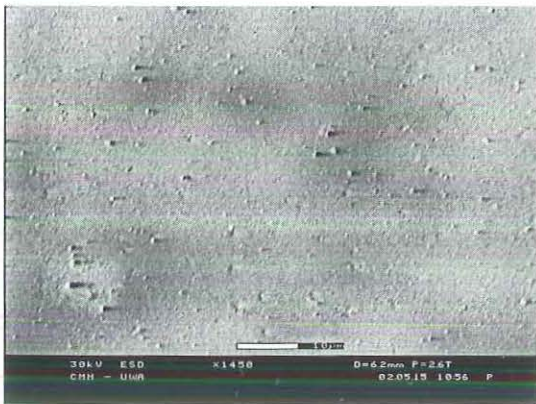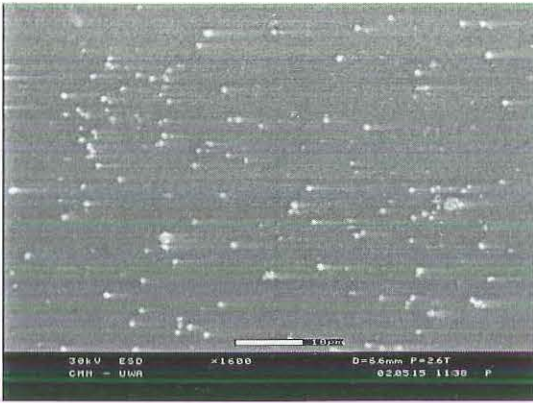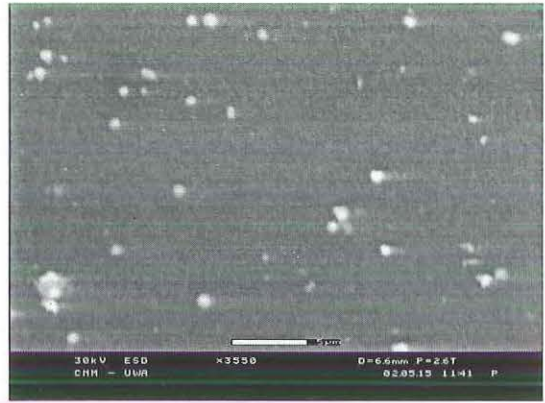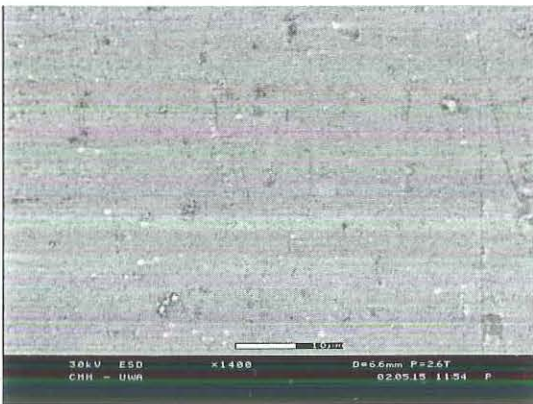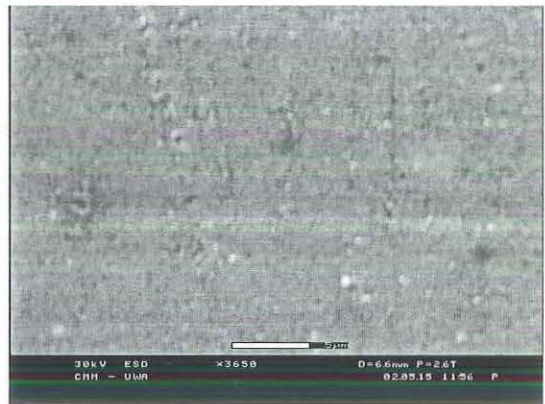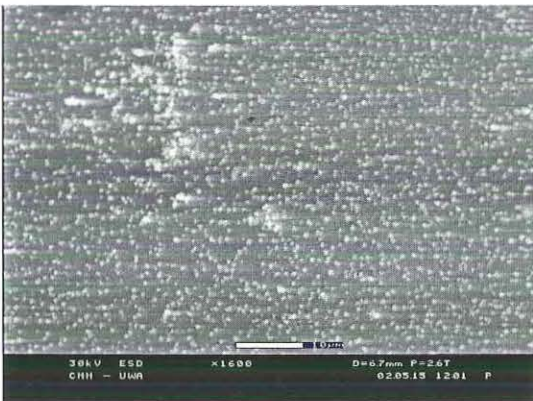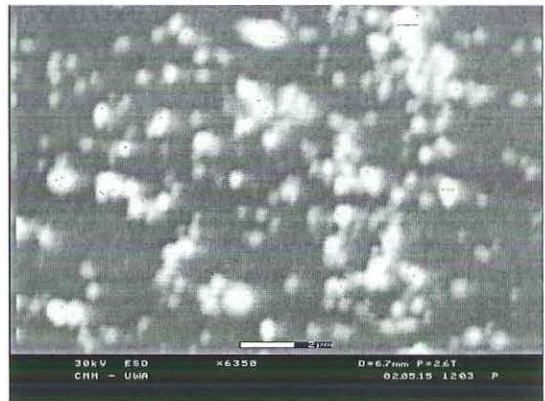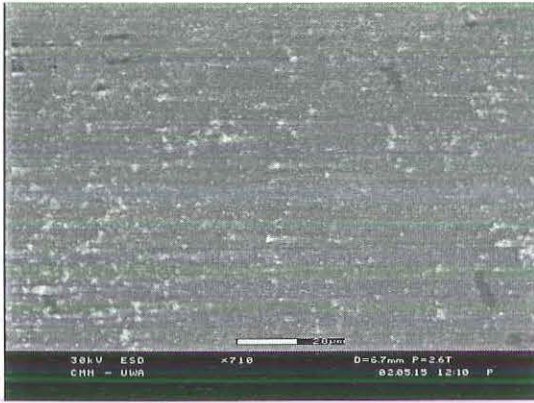Figure 5-5-33 Sample 14B
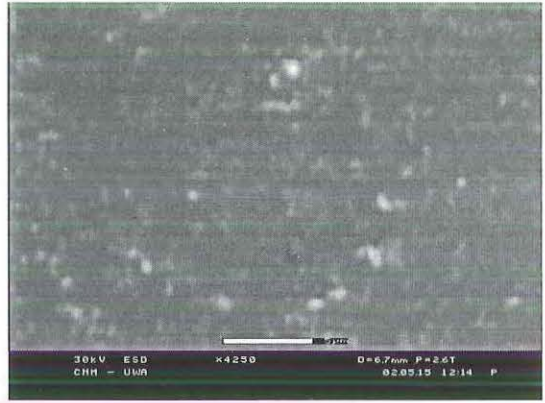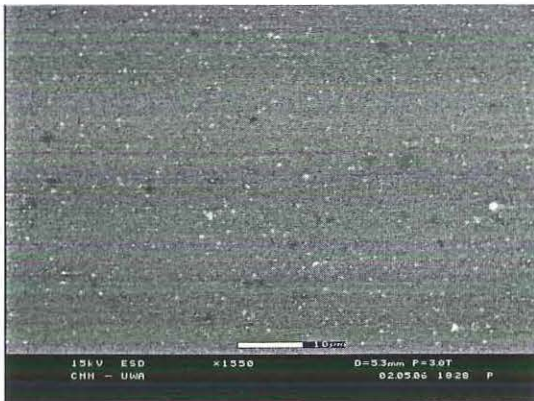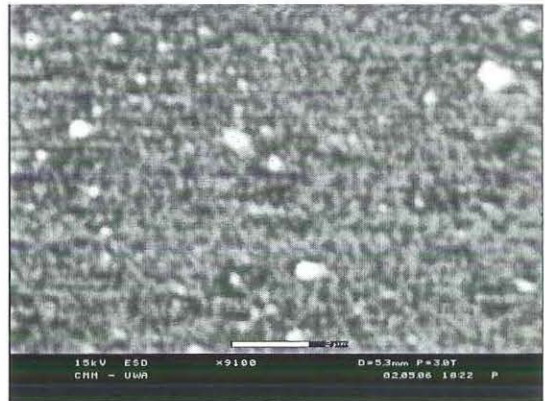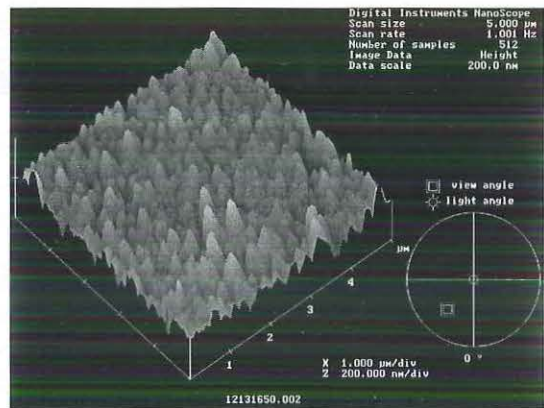

Figure 5-5-34 Sample 14E
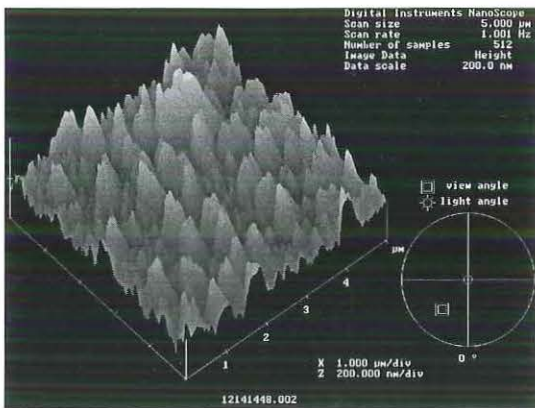
Figure 5-5-35 Sample 15B
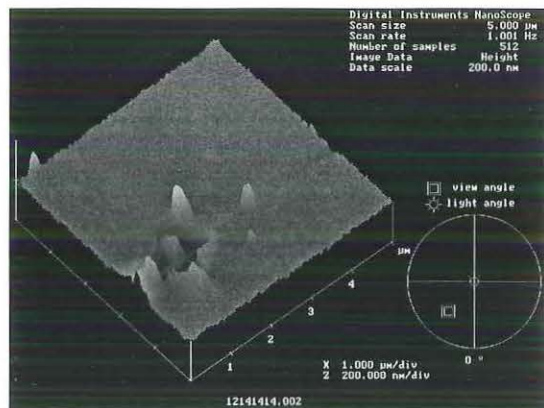
Figure 5-5-36 Sample 15E

5-6 Proton Induced X-ray Emission

The data obtained from the PIXE analysis is very anomalous, this is the result of two problems. Firstly, there was significant difficulty in obtaining any beam stability, due to recent technical difficulties and maintenance problems experienced by the 3MV accelerator used. Secondly, the Cadmium and Indium concentrations were determined using the L X-ray lines. These lines overlap and in some cases the analysis software may not be able to resolve the interference between them. The data from the PIXE has been summarised in Table 5-6-1. The stoichiometry has been arranged such that the values for Cadmium are all one, and the Sulfur and Indium values have been normalised with respect to Cadmium.

Table 5-6-1 Summary of PIXE data, showing the weight fraction and stoichiometry of Cadmium, Sulfur, and Indium.

Sample	Weight Fraction			Stoichiometry		
	Cd	S	In	Cd	S	In
04B	59%	9%	32%	1	0.53	0.54
05B	61%	14%	26%	1	0.79	0.41
06B	50%	12%	38%	1	0.87	0.75
07B	50%	10%	40%	1	0.69	0.77
08B	63%	15%	22%	1	0.85	0.35
09B	38%	11%	51%	1	1.01	1.34
10B	47%	9%	44%	1	0.69	0.93
11B	76%	17%	7%	1	0.78	0.10
12B	72%	17%	11%	1	0.82	0.15
13B	9%	8%	83%	1	3.11	9.15
14B	79%	14%	7%	1	0.64	0.08
15B	75%	16%	9%	1	0.74	0.11
04E	63%	11%	26%	1	0.62	0.41
05E	62%	15%	23%	1	0.86	0.35
06E	49%	13%	37%	1	0.96	0.74
07E	32%	7%	61%	1	0.80	1.88
08E	63%	15%	20%	1	0.83	0.31
09E	56%	15%	30%	1	0.93	0.52
10E	54%	10%	36%	1	0.64	0.66
11E	78%	17%	5%	1	0.78	0.06
12E	64%	17%	19%	1	0.94	0.29
13E	24%	10%	66%	1	1.52	2.68
14E	73%	16%	12%	1	0.75	0.16
15E	73%	18%	8%	1	0.84	0.11

This data indicates that there is a trend of decreasing Sulfur content in the CdS thin films with decreasing CBD temperature. This demonstrates that at higher temperatures, the Cadmium to Sulfur ratio is lower and the films have a decreased n-type nature due to less Sulfur donor levels being present in the band structure of the CdS thin films. The weight fraction stoichiometry of Indium shown in Table 5-6-1 are completely unreliable, as can be seen from samples 04 to 06 that were grown with no Indium dopant. Due to the anomalous nature of the data given by this PIXE analysis, no further determination can be made concerning the properties of the CdS thin films. It could be suggested that this analysis could be repeated when the facilities at ANSTO have been sufficiently repaired or at another facility that has more reliable equipment.

5-7 Electrical Measurements

A majority of the samples could not be electrically measured as the films were too thin or did not have a consistent coating on the substrate which in turn caused short circuit effects. The data for the electrical measurements was compiled and manipulated to give the resistance of the CdS thin samples in the dark, under illumination of a flash light, and under the illumination of a strobe light. A collection of the results under these conditions is shown in Table 5-7-1. This data gives a clear indication that the as-deposited CdS thin films have a lower resistance in the dark and under both types of illumination. The resistance does seem to decrease with increasing light intensity in both the as-deposited films and the annealed without much variation.

Table 5-7-1 Resistance measurements.

Flash Light		
Sample	Dark Resistance Ohms	Light Resistance Ohms
05C	5.6.E+10	2.5.E+10
05D	4.0.E+09	2.1.E+09
08C	1.7.E+10	4.0.E+09
08D	2.9.E+09	1.5.E+09
11C	5.2.E+10	2.2.E+10
11D	7.8.E+07	6.3.E+07

Strobe		
Sample	Dark Resistance Ohms	Light Resistance Ohms
05C	2.5E+10	1.6E+10
05D	7.4E+08	3.5E+08
08C	8.3E+09	1.5E+09
08D	8.9E+08	2.4E+08
11C	2.5E+10	8.9E+09
11D	1.0E+08	5.2E+07

DISCUSSION

An analysis of the SIMS data by making a comparison of depth profiles between annealed and as-deposited CdS thin films, shows the annealed films as having in the vicinity of 10 times more Oxygen present. The depth profiles also indicate that Cadmium and Sulfur present in both the as-deposited and annealed thin films is similar. The SIMS data also revealed that the comparative dopant concentrations between the CBD solution and the CdS thin film composition remained roughly constant. This is evidenced by the jump in Indium dopant concentration by a factor of almost 10 for corresponding films that had deposition solutions with Indium concentrations that differed by a factor of 10. The depth profiles constructed from the SIMS data provide evidence that suggests that the Indium concentration in the CdS thin films increases with depth as shown in Figure 5-3-9. This is presumed to be the effect of a decreasing Indium concentration left in the deposition solution as deposition of the thin films progresses.

The data in Figure 5-3-9 also suggests that annealed CdS thin films have a marginally higher Indium content than the corresponding as-deposited thin films. This may be the effect of decreasing Cadmium and Sulfur concentrations in the annealed films. It could also be an artifact of the SIMS analysis system where the annealed films sputter inconsistently compared to the as-deposited films.

Images obtained from CCI have indicated the presence of a protruding structure on the surface of the CdS thin films. These structures are, for the majority of cases, only present in the annealed films, and appear as bright spots that contrast quite clearly with the surrounding surface material. The size of the structures varies but are usually in the

region of ≤1μm across. Images from the AFM analysis also show nodule like structures present in the CCI analysis at the surface of the annealed CdS thin films, as shown in Figures 5-5-1 and 5-5-2. The data shows the nodules to be of a size of approximately 1μm across. The three dimensional surface plots constructed from the AFM images show the nodules to be in the vicinity of 200nm in height. These structures can not be attributed to the Indium doping as the nodules occur in both the doped and undoped films. This suggests that the structures are possibly composed of CdO or $CdSO_4$, as there is a corresponding increase in the Oxygen content of the films after annealing.

In addition the CCI images show evidence that the CdS thin films grown at higher deposition temperatures have increasingly irregular film surfaces. Such features include incomplete substrate coverage, and a large quantity of particulate adhered to the films surface, as seen in Figures 5-4-35, and 5-4-39. A smooth consistent film surface is obtainable from CdS thin films that are as-deposited and grown at lower temperatures, as seen in Figure 5-4-7. The AFM analysis agrees with the CCI analysis in that low temperature grown films have a smoother surface than those that grown at higher temperatures. This can be illustrated by comparing the low temperature grown film in Figures 5-5-3 and 5-5-4 with the high temperature grown films in Figures 5-5-23 and 5-5-24. The AFM analysis also indicates that the as-deposited films generally have smoother surface topography than the corresponding annealed films. This can be seen by making a comparison of Figures 5-5-31, 5-5-32 and Figures 5-5-35, 5-5-36. This could be due to the decreased frequency of the ion by ion deposition of CdS onto the substrate, and the increased frequency of the formation of colloidal particulates in solution that then adhere to the surface of the substrate disrupting the uniform growth of the film at increased deposition temperatures.

The PIXE analysis indicates that there is an increasing Sulfur deficiency in the CdS thin films grown at lower temperatures. Therefore, the Cadmium to Sulfur ratio is decreasing with increasing deposition temperature. This could be the result of more Sulfur ions being released from dissolved compounds ready for deposition at increased temperatures.

An analysis of the effects of illumination on the resistance of the CdS thin films has revealed that the as-deposited films have a lower resistance than those annealed in air. This data is inconsistent with that present in the current literature. The as deposited films should be more resistive than the annealed films. This may be due to problems with contacting the samples with the analysis circuit and the extremely thin films causing short circuit effects, rendering the data anomalous.

CONCLUSIONS

- Annealing of the CdS thin films in an air atmosphere increases the Oxygen content of the films constituents.

- Annealed CdS thin films also appear to have a slightly higher Indium dopant concentration.

- The dopant concentration in the CBD solution is proportional to the dopant concentration in the CdS thin film after deposition.

- The Indium dopant concentration is not constant with the depth of the CdS thin film and decreases with increasing thickness.

- The annealing of the CdS thin films develops nodule like structures at the surface of the film.

- The annealing process also decreases the smooth surface characteristic found in the as-deposited CdS thin film surfaces.

- CdS thin films grown at higher temperatures were shown to have more irregular surface features, in that incomplete coverage of the substrate was experienced as well as an increase in the amount of particulate adhered to the films surface.

- CdS thin films grown at lower deposition temperatures also had increased sulfur deficiencies.

- For future studies it is recommended that the nodule like structures present on the surfaces of the annealed CdS thin films be quantitatively examined to determine their composition relative to the rest of the film.

End

APPENDIX A: Materials Safety Data Sheets

Product Number: 289159
Product Name: Cadmium acetate, dihydrate, 98%

Valid 05/2002 - 07/2002

Sigma Aldrich Pty., Ltd.
2/14 Anella Avenue
Castle Hill NSW 2154 Australia
Phone: 61 2 9841 0555
Fax: 61 2 9841 0500
Email: ausmail@sial.com

MATERIAL SAFETY DATA SHEET

SECTION 1. - - - - - - - - - CHEMICAL IDENTIFICATION- - - - - - - - - -
    CATALOG #:   289159
    NAME: CADMIUM ACETATE DIHYDRATE, 98%
SECTION 2. - - - - - COMPOSITION/INFORMATION ON INGREDIENTS - - - - - -
    CAS #: 5743-04-4
    MF: C2H4O2
    SYNONYMS
    CADMIUM ACETATE DIHYDRATE * CADMIUM DIACETATE DIHYDRATE *
SECTION 3. - - - - - - - - - - HAZARDS IDENTIFICATION - - - - - - - - -
 LABEL PRECAUTIONARY STATEMENTS
  TOXIC
  MAY CAUSE CANCER.
  HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
  DANGER:
  CONTAINS CADMIUM.
  CANCER HAZARD.
  AVOID CREATING DUST.
  CAN CAUSE LUNG AND KIDNEY DISEASE.
  IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE
  IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
  WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE
  PROTECTION.
SECTION 4. - - - - - - - - - FIRST-AID MEASURES- - - - - - - - - - -
  IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS
  AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED
  CLOTHING AND SHOES.
  IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
  RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
  IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
  CALL A PHYSICIAN.
  DISCARD CONTAMINATED CLOTHING AND SHOES.
SECTION 5. - - - - - - - - - FIRE FIGHTING MEASURES - - - - - - - - - -
 EXTINGUISHING MEDIA
  WATER SPRAY.
  CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
 SPECIAL FIREFIGHTING PROCEDURES
  WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
  PREVENT CONTACT WITH SKIN AND EYES.
 UNUSUAL FIRE AND EXPLOSIONS HAZARDS
  EMITS TOXIC FUMES UNDER FIRE CONDITIONS.

SECTION 6. - - - - - - - ACCIDENTAL RELEASE MEASURES- - - - - - - - -
    EVACUATE AREA.
    WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY
    RUBBER GLOVES.
    WEAR DISPOSABLE COVERALLS AND DISCARD THEM AFTER USE.
    SWEEP UP, PLACE IN A BAG AND HOLD FOR WASTE DISPOSAL.
    VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.
SECTION 7. - - - - - - - - - HANDLING AND STORAGE- - - - - - - - - - -
    REFER TO SECTION 8.
SECTION 8. - - - - - - EXPOSURE CONTROLS/PERSONAL PROTECTION- - - - -
    WEAR APPROPRIATE NIOSH/MSHA-APPROVED RESPIRATOR, CHEMICAL-RESISTANT
    GLOVES, SAFETY GOGGLES, OTHER PROTECTIVE CLOTHING.
    SAFETY SHOWER AND EYE BATH.
    USE ONLY IN A CHEMICAL FUME HOOD.
    DO NOT BREATHE DUST.
    AVOID ALL CONTACT.
    WASH THOROUGHLY AFTER HANDLING.
    CARCINOGEN.
    HARMFUL SOLID.
    KEEP TIGHTLY CLOSED.
    STORE IN A COOL DRY PLACE.
SECTION 9. - - - - - - - PHYSICAL AND CHEMICAL PROPERTIES - - - - - - -
    APPEARANCE AND ODOR
    WHITE CRYSTALLINE POWDER
SECTION 10. - - - - - - - -STABILITY AND REACTIVITY - - - - - - - - -
    INCOMPATIBILITIES
    STRONG OXIDIZING AGENTS
    STRONG ACIDS
    STRONG BASES
    HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
    TOXIC FUMES OF:
    CARBON MONOXIDE, CARBON DIOXIDE
SECTION 11. - - - - - - - - - TOXICOLOGICAL INFORMATION - - - - - - - -
    ACUTE EFFECTS
    HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
    MAY CAUSE IRRITATION.
    CHRONIC EFFECTS
    CARCINOGEN.
    TARGET ORGAN(S):
    LUNGS
    KIDNEYS
    TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND
    TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.
    RTECS #: AF7505000
    ACETIC ACID, CADMIUM SALT, DIHYDRATE
    TOXICITY DATA
    ORL-RAT LD50:360 MG/KG   KHZDAN 22,168,1979
    ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES
    (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR
    COMPLETE INFORMATION.
SECTION 12. - - - - - - - - - ECOLOGICAL INFORMATION - - - - - - - - - -
    DATA NOT YET AVAILABLE.
SECTION 13. - - - - - - - - - DISPOSAL CONSIDERATIONS - - - - - - - - -
    CONTACT A LICENSED PROFESSIONAL WASTE DISPOSAL SERVICE TO DISPOSE OF
    THIS MATERIAL.
    OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.
SECTION 14. - - - - - - - - - -TRANSPORT INFORMATION - - - - - - - - -
    CONTACT ALDRICH CHEMICAL COMPANY FOR TRANSPORTATION INFORMATION.
SECTION 15. - - - - - - - - - REGULATORY INFORMATION - - - - - - - - - -
    EUROPEAN INFORMATION

CAUTION: SUBSTANCE NOT YET FULLY TESTED.
TOXIC
R 45
MAY CAUSE CANCER.
R 20/21/22
HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
S 45
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE
IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
S 36/37/39
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE
PROTECTION.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-TWA 0.01 MG(CD)/M3, INHALABLE DUST DTLVS* TLV/BEI,1999
ACGIH TLV-TWA 0.002 MG(CD)/M3, RESPIRABLE DUSTDTLVS* TLV/BEI,1999
ACGIH TLV-SUSPECTED HUMAN CARCINOGEN   DTLVS* TLV/BEI,1999
IARC CANCER REVIEW:HUMAN SUFFICIENT EVIDENCE IMEMDT 58,119,1993
IARC CANCER REVIEW:ANIMAL SUFFICIENT EVIDENCE IMEMDT 58,119,1993
IARC CANCER REVIEW:GROUP 1   IMEMDT 58,119,1993
MSHA STANDARD-AIR:TWA 0.2 MG(CD)/M3
 DTLVS* 3,34,1971
OEL-ARAB REPUBLIC OF EGYPT: TWA 0.05 MG(CD)/M3, JAN1993
OEL-AUSTRALIA: TWA 0.05 MG(CD)/M3, JAN1993
OEL-AUSTRIA: CARCINOGEN, JAN1999
OEL-BELGIUM: TWA 0.05 MG(CD)/M3, JAN1993
OEL-DENMARK: TWA 0,01 MG(CD)/M3, JAN1999
OEL-FINLAND: TWA 0.02 MG(CD)/M3, CARCINOGEN, JAN1999
OEL-FRANCE: VME 0.05 MG(CD)/M3, JAN1999
OEL-GERMANY: CARCINOGEN, JAN1999
OEL-INDIA: TWA 0.05 MG(CD)/M3, JAN1993
OEL-JAPAN: OEL 0.05 MG(CD)/M3, GROUP 1 CARCINOGEN, JAN1999
OEL-NORWAY: TWA 0.05 MG(CD)/M3, JAN1999
OEL-THE PHILIPPINES: TWA 0.2 MG(CD)/M3, JAN1993
OEL-POLAND: MAC(TWA)FUME 0.02 MG(CD)/M3, MAC(STEL) FUME 0.05 MG(CD)/M3,
 JAN1999
OEL-POLAND: MAC(TWA) DUST 0.04 MG(CD)/M3, MAC(STEL) DUST 0.2 MG(CD)/M3,
 JAN1999
OEL-RUSSIA: TWA 0.01 MG(CD)/M3, STEL 0.05 MG(CD)/M3, JAN1993
OEL-SWEDEN: NGV 0.02 MG(CD)/M3, CARCINOGEN, JAN1999
OEL-SWITZERLAND: MAK-W 0.05 MG(CD)/M3, CARCINOGEN, JAN1999
OEL-THAILAND: TWA 0.2 MG(CD)/M3, STEL 0.5 MG(CD)/M3, JAN1993
OEL-TURKEY: TWA 0.2 MG(CD)/M3, JAN1993
OEL-UNITED KINGDOM: TWA 0.025 MG(CD)/M3, SEP2000
OEL IN ARGENTINA, BULGARIA, COLOMBIA, JORDAN, KOREA CHECK ACGIH TLV;
OEL IN NEW ZEALAND, SINGAPORE, VIETNAM CHECK ACGIH TLV
U.S. INFORMATION
THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.
SECTION 16.---------OTHER INFORMATION-----------
THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO
BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA, ALDRICH,
FLUKA SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING
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Product Number: T33553
Product Name: Thiourea, 99%

MATERIAL SAFETY DATA SHEET

SECTION 1. - - - - - - - - - CHEMICAL IDENTIFICATION- - - - - - - - - -
    CATALOG #:   T33553
    NAME: THIOUREA, 99%
SECTION 2. - - - - - COMPOSITION/INFORMATION ON INGREDIENTS - - - - - -
    CAS #:   62-56-6
    MF: CH4N2S
    EC NO: 200-543-5
   SYNONYMS
   ISOTHIOUREA * PSEUDOTHIOUREA * RCRA WASTE NUMBER U219 * SULOUREA *
   THIOCARBAMIDE * THIOCARBONIC ACID DIAMIDE * THIOMOCOVINA (CZECH) *
   BETA-THIOPSEUDOUREA * 2-THIOPSEUDOUREA * THIOUREA * 2-THIOUREA * THU *
   TSIZP 34 * UREA, THIO- (8CI) * USAF EK-497 *
SECTION 3. - - - - - - - - - - HAZARDS IDENTIFICATION - - - - - - - - -
  LABEL PRECAUTIONARY STATEMENTS
  TOXIC
  DANGEROUS FOR THE ENVIRONMENT
  TOXIC IF SWALLOWED.
  POSSIBLE RISK OF IRREVERSIBLE EFFECTS.
  IRRITATING TO SKIN.
  MAY CAUSE SENSITIZATION BY SKIN CONTACT.
  TOXIC TO AQUATIC ORGANISMS, MAY CAUSE LONG-TERM ADVERSE EFFECTS
  IN THE AQUATIC ENVIRONMENT.
  POSSIBLE CARCINOGEN (US)
  TARGET ORGAN(S):
  LIVER
  THYROID
  CALIF. PROP. 65 CARCINOGEN.
  IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF
  WATER AND SEEK MEDICAL ADVICE.
  WEAR SUITABLE PROTECTIVE CLOTHING AND GLOVES.
  AVOID RELEASE TO THE ENVIRONMENT. REFER TO SPECIAL INSTRUCTIONS/
  SAFETY DATA SHEETS.
SECTION 4. - - - - - - - - - - FIRST-AID MEASURES- - - - - - - - - - -
  IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
  CALL A PHYSICIAN IMMEDIATELY.
  IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
  RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
  IN CASE OF SKIN CONTACT, FLUSH WITH COPIOUS AMOUNTS OF WATER
  FOR AT LEAST 15 MINUTES. REMOVE CONTAMINATED CLOTHING AND
  SHOES. CALL A PHYSICIAN.
  IN CASE OF CONTACT WITH EYES, FLUSH WITH COPIOUS AMOUNTS OF WATER
  FOR AT LEAST 15 MINUTES. ASSURE ADEQUATE FLUSHING BY SEPARATING
  THE EYELIDS WITH FINGERS. CALL A PHYSICIAN.
SECTION 5. - - - - - - - - - FIRE FIGHTING MEASURES - - - - - - - - - -
  EXTINGUISHING MEDIA
   WATER SPRAY.

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CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
SPECIAL FIREFIGHTING PROCEDURES
 WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
 PREVENT CONTACT WITH SKIN AND EYES.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
 EMITS TOXIC FUMES UNDER FIRE CONDITIONS.
SECTION 6. - - - - - - - - ACCIDENTAL RELEASE MEASURES- - - - - - - - -
 WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY
 RUBBER GLOVES.
 SWEEP UP, PLACE IN A BAG AND HOLD FOR WASTE DISPOSAL.
 AVOID RAISING DUST.
 VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.
 EVACUATE AREA.
SECTION 7. - - - - - - - - - - HANDLING AND STORAGE- - - - - - - - - - -
 REFER TO SECTION 8.
SECTION 8. - - - - - - EXPOSURE CONTROLS/PERSONAL PROTECTION- - - - - -
 USE ONLY IN A CHEMICAL FUME HOOD.
 SAFETY SHOWER AND EYE BATH.
 WASH CONTAMINATED CLOTHING BEFORE REUSE.
 WASH THOROUGHLY AFTER HANDLING.
 DO NOT BREATHE DUST.
 DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
 AVOID PROLONGED OR REPEATED EXPOSURE.
 NIOSH/MSHA-APPROVED RESPIRATOR.
 COMPATIBLE CHEMICAL-RESISTANT GLOVES.
 CHEMICAL SAFETY GOGGLES.
 KEEP TIGHTLY CLOSED.
 STORE IN A COOL DRY PLACE.
SECTION 9. - - - - - - - PHYSICAL AND CHEMICAL PROPERTIES - - - - - - -
 PHYSICAL PROPERTIES
  MELTING POINT: 174 - 177 C
SECTION 10. - - - - - - - - -STABILITY AND REACTIVITY - - - - - - - - -
 STABILITY
  STABLE.
 INCOMPATIBILITIES
  HEAT
  STRONG OXIDIZING AGENTS
  STRONG ACIDS
  STRONG BASES
 HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
  CARBON MONOXIDE, CARBON DIOXIDE
  NITROGEN OXIDES
  SULFUR OXIDES
 HAZARDOUS POLYMERIZATION
  WILL NOT OCCUR.
SECTION 11. - - - - - - - - - TOXICOLOGICAL INFORMATION - - - - - - - -
 ACUTE EFFECTS
  CAUSES SKIN IRRITATION.
  MAY BE HARMFUL IF ABSORBED THROUGH THE SKIN.
  MAY CAUSE EYE IRRITATION.
  MAY BE HARMFUL IF INHALED.
  MATERIAL MAY BE IRRITATING TO MUCOUS MEMBRANES AND UPPER
  RESPIRATORY TRACT.
  TOXIC IF SWALLOWED.
  MAY CAUSE ALLERGIC SKIN REACTION.
 CHRONIC EFFECTS
  THIS PRODUCT IS OR CONTAINS A COMPONENT THAT HAS BEEN REPORTED TO BE
  POSSIBLY CARCINOGENIC BASED ON ITS IARC, ACGIH, NTP OR EPA
  CLASSIFICATION.
  TARGET ORGAN(S):

LIVER
THYROID
BONE MARROW
POSSIBLE RISK OF CONGENITAL MALFORMATION IN THE FETUS.
RTECS #: YU2800000
UREA, 2-THIO-
IRRITATION DATA
EYE-RBT 14%   GTPZAB 30(3),42,1986
TOXICITY DATA
  UNR-MAN LDLO:147 MG/KG   85DCAI 2,73,1970
  ORL-RAT LD50:125 MG/KG   HBTXAC 5,177,1959
  IPR-RAT LD50:436 MG/KG   FCTXAV 3,597,1965
  IPR-MUS LD50:100 MG/KG   NTIS** AD277-689
  IPR-MAM LD50:3500 MG/KG   GTPZAB 30(3),42,1986
TARGET ORGAN DATA
  LUNGS, THORAX OR RESPIRATION (OTHER CHANGES)
  LIVER (MULTIPLE EFFECTS)
  BLOOD (HEMORRHAGE)
  BLOOD (GRANULOCYTOPENIA)
  BLOOD (CHANGES IN CELL COUNT)
  EFFECTS ON FERTILITY (POST-IMPLANTATION MORTALITY)
  SPECIFIC DEVELOPMENTAL ABNORMALITIES (CENTRAL NERVOUS SYSTEM)
  SPECIFIC DEVELOPMENTAL ABNORMALITIES (MUSCULOSKELETAL SYSTEM)
  SPECIFIC DEVELOPMENTAL ABNORMALITIES (ENDOCRINE SYSTEM)
  TUMORIGENIC (EQUIVOCAL TUMORIGENIC AGENT BY RTECS CRITERIA)
 ADDITIONAL INFORMATION
  ORL-RAT LD50:1750 MG/KG
  SKN-RBT LD50:>2800 MG/KG
  ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES
  (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR
  COMPLETE INFORMATION.
SECTION 12. - - - - - - - - ECOLOGICAL INFORMATION - - - - - - - - - -
  DATA NOT YET AVAILABLE.
SECTION 13. - - - - - - - - DISPOSAL CONSIDERATIONS - - - - - - - - -
  CONTACT A LICENSED PROFESSIONAL WASTE DISPOSAL SERVICE TO DISPOSE OF
  THIS MATERIAL.
  DISSOLVE OR MIX THE MATERIAL WITH A COMBUSTIBLE SOLVENT AND BURN IN A
  CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER.
  OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.
SECTION 14. - - - - - - - - - TRANSPORT INFORMATION - - - - - - - - -
  CONTACT ALDRICH CHEMICAL COMPANY FOR TRANSPORTATION INFORMATION.
SECTION 15. - - - - - - - - - REGULATORY INFORMATION - - - - - - - - -
  EUROPEAN INFORMATION
  EC INDEX NO: 612-082-00-0
  TOXIC
  DANGEROUS FOR THE ENVIRONMENT
  R 22
  HARMFUL IF SWALLOWED.
  R 40
  POSSIBLE RISK OF IRREVERSIBLE EFFECTS.
  R 51/53
  TOXIC TO AQUATIC ORGANISMS, MAY CAUSE LONG-TERM ADVERSE EFFECTS
  IN THE AQUATIC ENVIRONMENT.
  R 63
  POSSIBLE RISK OF HARM TO THE UNBORN CHILD.
  S 36/37
  WEAR SUITABLE PROTECTIVE CLOTHING AND GLOVES.
  S 61
  AVOID RELEASE TO THE ENVIRONMENT. REFER TO SPECIAL INSTRUCTIONS/
  SAFETY DATA SHEETS.

REVIEWS, STANDARDS, AND REGULATIONS
 OEL=MAK
 IARC CANCER REVIEW:ANIMAL SUFFICIENT EVIDENCE IMEMDT 7,95,1974
 IARC CANCER REVIEW:HUMAN NO ADEQUATE DATA   IMEMDT 7,95,1974
 IARC CANCER REVIEW:GROUP 2B   IMSUDL 7,56,1987
 OEL-AUSTRIA: SUSPECTED CARCINOGEN, JAN1999
 OEL-FINLAND: CARCINOGEN, JAN1999
 OEL-FRANCE: CARCINOGEN, JAN1993
 OEL-GERMANY: CARCINOGEN, JAN1999
 OEL-RUSSIA: STEL 0.3 MG/M3, JAN1993
 OEL-SWEDEN: CARCINOGEN, JAN1999
 NOHS 1974: HZD 82272; NIS 29; TNF 1179; NOS 25; TNE 12517
 NOES 1983: HZD 82272; NIS 50; TNF 2999; NOS 57; TNE 37571; TFE 10969
 EPA GENETOX PROGRAM 1988, POSITIVE: CARCINOGENICITY-MOUSE/RAT; CELL
  TRANSFORM.-SA7/F344 RAT
 EPA GENETOX PROGRAM 1988, POSITIVE: SHE-CLONAL ASSAY; CELL
  TRANSFORM.-RLV F344 RAT EMBRYO
 EPA GENETOX PROGRAM 1988, POSITIVE: HOST-MEDIATED ASSAY
 EPA GENETOX PROGRAM 1988, NEGATIVE: CELL TRANSFORM.-SA7/SHE; E COLI
  POLA WITH S9
 EPA GENETOX PROGRAM 1988, NEGATIVE: HISTIDINE REVERSION-AMES TEST;
  SPERM MORPHOLOGY-MOUSE
 EPA GENETOX PROGRAM 1988, NEGATIVE: S CEREVISIAE-HOMOZYGOSIS
 EPA GENETOX PROGRAM 1988, INCONCLUSIVE: E COLI POLA WITHOUT S9
 EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
 EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JANUARY 2001
 NTP 9TH REPORT ON CARCINOGENS,2000:REASONABLY ANTICIPATED TO BE HUMAN
  CARCINOGEN
 U.S. INFORMATION
 THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.
 CALIFORNIA PROPOSITION 65:
 THIS PRODUCT IS OR CONTAINS CHEMICAL(S) KNOWN TO THE STATE OF
 CALIFORNIA TO CAUSE CANCER.
SECTION 16. - - - - - - - - - - OTHER INFORMATION- - - - - - - - - - - -
 THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO
 BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA, ALDRICH,
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Product Number: 334073
Product Name: Indium(III) chloride, tetrahydrate, 97%

Valid 05/2002 - 07/2002

Sigma Aldrich Pty., Ltd.
2/14 Anella Avenue
Castle Hill NSW 2154 Australia
Phone: 61 2 9841 0555
Fax: 61 2 9841 0500
Email: ausmail@sial.com

            M A T E R I A L S A F E T Y D A T A S H E E T

SECTION 1. - - - - - - - - CHEMICAL IDENTIFICATION- - - - - - - - -

CATALOG #:   334073
NAME: INDIUM(III) CHLORIDE TETRAHYDRATE, 97%
SECTION 2. - - - - - COMPOSITION/INFORMATION ON INGREDIENTS - - - - -
CAS #: 22519-64-8
MF: CL3IN
SYNONYMS
INDIUM TRICHLORIDE TETRAHYDRATE *
SECTION 3. - - - - - - - - - HAZARDS IDENTIFICATION - - - - - - - - -
LABEL PRECAUTIONARY STATEMENTS
HIGHLY TOXIC (USA)
TOXIC (EU)
TOXIC BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
CAUSES BURNS.
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE
IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF
WATER AND SEEK MEDICAL ADVICE.
DO NOT BREATHE DUST.
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE
PROTECTION.
MOISTURE SENSITIVE
KEEP TIGHTLY CLOSED.
SECTION 4. - - - - - - - - - FIRST-AID MEASURES- - - - - - - - - - -
IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS
AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED
CLOTHING AND SHOES.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN IMMEDIATELY.
WASH CONTAMINATED CLOTHING BEFORE REUSE.
SECTION 5. - - - - - - - - - FIRE FIGHTING MEASURES - - - - - - - - - -
EXTINGUISHING MEDIA
NONCOMBUSTIBLE.
USE EXTINGUISHING MEDIA APPROPRIATE TO SURROUNDING FIRE CONDITIONS.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
PREVENT CONTACT WITH SKIN AND EYES.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
EMITS TOXIC FUMES UNDER FIRE CONDITIONS.
SECTION 6. - - - - - - - - ACCIDENTAL RELEASE MEASURES- - - - - - - - -
EVACUATE AREA.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY
RUBBER GLOVES.
SWEEP UP, PLACE IN A BAG AND HOLD FOR WASTE DISPOSAL.
AVOID RAISING DUST.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.
SECTION 7. - - - - - - - - - HANDLING AND STORAGE- - - - - - - - - - -
REFER TO SECTION 8.
SECTION 8. - - - - - - EXPOSURE CONTROLS/PERSONAL PROTECTION- - - - - -
WEAR APPROPRIATE NIOSH/MSHA-APPROVED RESPIRATOR, CHEMICAL-RESISTANT
GLOVES, SAFETY GOGGLES, OTHER PROTECTIVE CLOTHING.
SAFETY SHOWER AND EYE BATH.
USE ONLY IN A CHEMICAL FUME HOOD.
DO NOT BREATHE DUST.
AVOID CONTACT WITH EYES, SKIN AND CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
HIGHLY TOXIC.
CORROSIVE.

KEEP TIGHTLY CLOSED.
MOISTURE SENSITIVE
STORE IN A COOL DRY PLACE.
SECTION 9. - - - - - - PHYSICAL AND CHEMICAL PROPERTIES - - - - - -
APPEARANCE AND ODOR
WHITE TO OFF-WHITE CRYSTALLINE CHUNKS
SECTION 10. - - - - - - - - STABILITY AND REACTIVITY - - - - - - - - -
INCOMPATIBILITIES
STRONG ACIDS
MAY DECOMPOSE ON EXPOSURE TO MOIST AIR OR WATER.
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
HYDROGEN CHLORIDE GAS
SECTION 11. - - - - - - - - - TOXICOLOGICAL INFORMATION - - - - - - - -
ACUTE EFFECTS
MAY BE FATAL IF INHALED, SWALLOWED, OR ABSORBED THROUGH SKIN.
MATERIAL IS EXTREMELY DESTRUCTIVE TO TISSUE OF THE MUCOUS MEMBRANES
AND UPPER RESPIRATORY TRACT, EYES AND SKIN.
INHALATION MAY RESULT IN SPASM, INFLAMMATION AND EDEMA OF THE
LARYNX AND BRONCHI, CHEMICAL PNEUMONITIS AND PULMONARY EDEMA.
SYMPTOMS OF EXPOSURE MAY INCLUDE BURNING SENSATION, COUGHING,
WHEEZING, LARYNGITIS, SHORTNESS OF BREATH, HEADACHE, NAUSEA AND
VOMITING.
TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND
TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.
RTECS #: NL1430000
INDIUM CHLORIDE, TETRAHYDRATE
TOXICITY DATA
IPR-MUS LD50:12 MG/KG   TXAPA9 63,461,1982
ADDITIONAL INFORMATION
ACGIH TLV-TWA: 0.1 MG/M3, INDIUM COMPOUNDS AS INDIUM. OSHA PEL: 8H
TWA 0.1 MG/M3, INDIUM COMPOUNDS.
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES
(RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR
COMPLETE INFORMATION.
SECTION 12. - - - - - - - - - ECOLOGICAL INFORMATION - - - - - - - - - -
DATA NOT YET AVAILABLE.
SECTION 13. - - - - - - - - - DISPOSAL CONSIDERATIONS - - - - - - - - -
THE MATERIAL SHOULD BE DISSOLVED IN 1) WATER; 2) ACID SOLUTION OR 3)
OXIDIZED TO A WATER-SOLUBLE STATE. PRECIPITATE THE MATERIAL AS THE
SULFIDE, ADJUSTING THE PH OF THE SOLUTION TO 7 TO COMPLETE PRE-
CIPITATION. FILTER THE INSOLUBLES AND DISPOSE OF THEM IN A HAZARDOUS-
WASTE SITE. DESTROY ANY EXCESS SULFIDE WITH SODIUM HYPOCHLORITE.
NEUTRALIZE THE SOLUTION BEFORE FLUSHING DOWN THE DRAIN.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.
SECTION 14. - - - - - - - - - - TRANSPORT INFORMATION - - - - - - - - -
CONTACT ALDRICH CHEMICAL COMPANY FOR TRANSPORTATION INFORMATION.
SECTION 15. - - - - - - - - - REGULATORY INFORMATION - - - - - - - - - -
EUROPEAN INFORMATION
CAUTION: SUBSTANCE NOT YET FULLY TESTED.
TOXIC
R 23/24/25
TOXIC BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
R 34
CAUSES BURNS.
S 45
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE
IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
S 26
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF
WATER AND SEEK MEDICAL ADVICE.

S 22
DO NOT BREATHE DUST.
S 36/37/39
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE
PROTECTION.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
OEL-UNITED KINGDOM: TWA 0.1 MG(IN)/M3, STEL 0.3 MG(IN)/M3, SEP2000
SECTION 16. - - - - - - - - - - OTHER INFORMATION- - - - - - - - - - -
THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO
BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA, ALDRICH,
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Product Number: 208183
Product Name: Cadmium sulfide

Valid 05/2002 - 07/2002

Sigma Aldrich Pty., Ltd.
2/14 Anella Avenue
Castle Hill NSW 2154 Australia
Phone: 61 2 9841 0555
Fax: 61 2 9841 0500
Email: ausmail@sial.com

MATERIAL SAFETY DATA SHEET

SECTION 1. - - - - - - - - - CHEMICAL IDENTIFICATION- - - - - - - - - -
CATALOG #:   208183
NAME: CADMIUM SULFIDE
SECTION 2. - - - - - COMPOSITION/INFORMATION ON INGREDIENTS - - - - - -
CAS #: 1306-23-6
MF: CDS
EC NO: 215-147-8
SYNONYMS
CADMIUM GOLDEN 366 * CADMIUM LEMON YELLOW 527 * CADMIUM MONOSULFIDE *
CADMIUM ORANGE * CADMIUM PRIMROSE 819 * CADMIUM SULPHIDE * CADMIUM
YELLOW * CADMIUM YELLOW 000 * CADMIUM YELLOW 892 * CADMIUM YELLOW
CONC. DEEP * CADMIUM YELLOW CONC. GOLDEN * CADMIUM YELLOW CONC. LEMON
* CADMIUM YELLOW CONC. PRIMROSE * CADMIUM YELLOW 10G CONC * CADMIUM
YELLOW OZ DARK * CADMIUM YELLOW PRIMROSE 47-4100 * CADMOPUR GOLDEN
YELLOW N * CADMOPUR YELLOW * CAPSEBON * C.P. GOLDEN YELLOW 55 * FERRO
LEMON YELLOW * FERRO ORANGE YELLOW * FERRO YELLOW * GREENOCKITE * GSK
* NCI-C02711 * PC 108 * PRIMROSE 1466 *
SECTION 3. - - - - - - - - - - HAZARDS IDENTIFICATION - - - - - - - - -
LABEL PRECAUTIONARY STATEMENTS
TOXIC
MAY CAUSE CANCER.
HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
DANGER:
CANCER HAZARD.
CAN CAUSE LUNG AND KIDNEY DISEASE.
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE

IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF
WATER AND SEEK MEDICAL ADVICE.
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE
PROTECTION.
SECTION 4. - - - - - - - - - - FIRST-AID MEASURES- - - - - - - - - - -
IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS
AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED
CLOTHING AND SHOES.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
SECTION 5. - - - - - - - - - FIRE FIGHTING MEASURES - - - - - - - - - -
 EXTINGUISHING MEDIA
  NONCOMBUSTIBLE.
  USE EXTINGUISHING MEDIA APPROPRIATE TO SURROUNDING FIRE CONDITIONS.
 SPECIAL FIREFIGHTING PROCEDURES
  WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
  PREVENT CONTACT WITH SKIN AND EYES.
 UNUSUAL FIRE AND EXPLOSIONS HAZARDS
  EMITS TOXIC FUMES UNDER FIRE CONDITIONS.
SECTION 6. - - - - - - - - ACCIDENTAL RELEASE MEASURES- - - - - - - - -
  EVACUATE AREA.
  WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BC· ,S AND HEAVY
  RUBBER GLOVES.
  WEAR DISPOSABLE COVERALLS AND DISCARD THEM AFTER USE.
  SWEEP UP, PLACE IN A BAG AND HOLD FOR WASTE DISPOSAL.
  AVOID RAISING DUST.
SECTION 7. - - - - - - - - - - HANDLING AND STORAGE- - - - - - - - - - -
  REFER TO SECTION 8.
SECTION 8. - - - - - - EXPOSURE CONTROLS/PERSONAL PROTECTION- - - - - -
  WEAR APPROPRIATE NIOSH/MSHA-APPROVED RESPIRATOR, CHEMICAL-RESISTANT
  GLOVES, SAFETY GOGGLES, OTHER PROTECTIVE CLOTHING.
  USE ONLY IN A CHEMICAL FUME HOOD.
  SAFETY SHOWER AND EYE BATH.
  DO NOT BREATHE DUST.
  DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
  AVOID PROLONGED OR REPEATED EXPOSURE.
  WASH THOROUGHLY AFTER HANDLING.
  WASH CONTAMINATED CLOTHING BEFORE REUSE.
  IRRITANT.
  KEEP TIGHTLY CLOSED.
  STORE IN A COOL DRY PLACE.
SECTION 9. - - - - - - - PHYSICAL AND CHEMICAL PROPERTIES - - - - - - -
 APPEARANCE AND ODOR
  ORANGE POWDER
 PHYSICAL PROPERTIES
  SPECIFIC GRAVITY: 4.820
SECTION 10. - - - - - - - - -STABILITY AND REACTIVITY - - - - - - - - -
 INCOMPATIBILITIES
  STRONG OXIDIZING AGENTS
SECTION 11. - - - - - - - - - TOXICOLOGICAL INFORMATION - - - - - - - -
 ACUTE EFFECTS
  DAMAGE TO THE LUNGS
  DAMAGE TO THE LIVER
  DAMAGE TO THE KIDNEYS
  EXPOSURE CAN CAUSE:
  HARMFUL IF INHALED OR SWALLOWED.
  CAUSES IRRITATION.
 CHRONIC EFFECTS
  CARCINOGEN.

TARGET ORGAN(S):
DAMAGE TO THE LUNGS
DAMAGE TO THE LIVER
DAMAGE TO THE KIDNEYS
KIDNEYS
LUNGS
RTECS #: EV3150000
CADMIUM SULFIDE
TOXICITY DATA
ORL-RAT LD50:7080 MG/KG   41HTAH -,14,1978
ORL-MUS LD50:1166 MG/KG   41HTAH -,14,1978
TARGET ORGAN DATA
BLOOD (LYMPHOMA INCLUDING HODGKIN'S DISEASE)
TUMORIGENIC (CARCINOGENIC BY RTECS CRITERIA)
TUMORIGENIC (EQUIVOCAL TUMORIGENIC AGENT BY RTECS CRITERIA)
TUMORIGENIC (TUMORS AT SITE OF APPLICATION)
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES
(RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR
COMPLETE INFORMATION.
SECTION 12. - - - - - - - - - ECOLOGICAL INFORMATION - - - - - - - - - -
DATA NOT YET AVAILABLE.
SECTION 13. - - - - - - - - - DISPOSAL CONSIDERATIONS - - - - - - - - - -
BURY IN A LANDFILL SITE APPROVED FOR THE DISPOSAL OF CHEMICAL
AND HAZARDOUS WASTES.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.
SECTION 14. - - - - - - - - - - TRANSPORT INFORMATION - - - - - - - - -
CONTACT ALDRICH CHEMICAL COMPANY FOR TRANSPORTATION INFORMATION.
SECTION 15. - - - - - - - - - REGULATORY INFORMATION - - - - - - - - - -
EUROPEAN INFORMATION
EC INDEX NO: 048-010-00-4
TOXIC
R 22
HARMFUL IF SWALLOWED.
R 40
POSSIBLE RISK OF IRREVERSIBLE EFFECTS.
R 48/23/25
TOXIC: DANGER OF SERIOUS DAMAGE TO HEALTH BY PROLONGED EXPOSURE
THROUGH INHALATION AND IF SWALLOWED.
S 22
DO NOT BREATHE DUST.
S 36/37
WEAR SUITABLE PROTECTIVE CLOTHING AND GLOVES.
S 45
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE
IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-TWA 0.01 MG(CD)/M3, INHALABLE DUST DTLVS* TLV/BEI,1999
ACGIH TLV-TWA 0.002 MG(CD)/M3, RESPIRABLE DUSTDTLVS* TLV/BEI,1999
ACGIH TLV-SUSPECTED HUMAN CARCINOGEN DTLVS* TLV/BEI,1999
IARC CANCER REVIEW:ANIMAL SUFFICIENT EVIDENCE IMEMDT 2,74,1973
IARC CANCER REVIEW:ANIMAL SUFFICIENT EVIDENCE IMEMDT 11,39,1976
IARC CANCER REVIEW:ANIMAL SUFFICIENT EVIDENCE IMEMDT 58,119,1993
IARC CANCER REVIEW:HUMAN SUFFICIENT EVIDENCE IMEMDT 58,119,1993
IARC CANCER REVIEW:GROUP 1   IMEMDT 58,119,1993
MSHA STANDARD-AIR:TWA 0.2 MG(CD)/M3
DTLVS* 3,34,1971
OEL-ARAB REPUBLIC OF EGYPT: TWA 0.05 MG(CD)/M3, JAN1993
OEL-AUSTRALIA: TWA 0.05 MG(CD)/M3, JAN1993
OEL-AUSTRIA: CARCINOGEN, JAN1999

OEL-BELGIUM: TWA 0.05 MG(CD)/M3, JAN1993
OEL-DENMARK: TWA 0.01 MG(CD)/M3, JAN1999
OEL-FINLAND: TWA 0.02 MG(CD)/M3, CARCINOGEN, JAN1999
OEL-FRANCE: VME 0.05 MG(CD)/M3, JAN1999
OEL-GERMANY: CARCINOGEN, JAN1999
OEL-INDIA: TWA 0.05 MG(CD)/M3, JAN1993
OEL-JAPAN: OEL 0.05 MG(CD)/M3, GROUP 1 CARCINOGEN, JAN1999
OEL-THE NETHERLANDS: MAC-TGG 0.02 MG(CD)/M3, MAC-K 0.1 MG(CD)/M3,
JAN1999
OEL-NORWAY: TWA 0.05 MG(CD)/M3, JAN1999
OEL-THE PHILIPPINES: TWA 0.2 MG(CD)/M3, JAN1993
OEL-POLAND: MAC(TWA) FUME 0.02 MG(CD)/M3, MAC(STEL) FUME 0.05
MG(CD)/M3, JAN1999
OEL-POLAND: MAC(TWA) DUST 0.04 MG(CD)/M3, MAC(STEL) DUST 0.2 MG(CD)/M3,
JAN1999
OEL-RUSSIA: TWA 0.01 MG(CD)/M3, STEL 0.05 MG(CD)/M3, JAN1993
OEL-SWEDEN: CARCINOGEN, JAN1999
OEL-SWITZERLAND: MAK-W 0.05 MG(CD)/M3, CARCINOGEN, JAN1999
OEL-THAILAND: TWA 0.2 MG(CD)/M3, STEL 0.5 MG(CD)/M3, JAN1993
OEL-TURKEY: TWA 0.2 MG(CD)/M3, JAN1993
OEL-UNITED KINGDOM: TWA 0.03 MG(CD)/M3, SEP2000
OEL IN ARGENTINA, BULGARIA, COLOMBIA, JORDAN, KOREA CHECK ACGIH TLV;
OEL IN NEW ZEALAND, SINGAPORE, VIETNAM CHECK ACGIH TLV
NIOSH REL TO CADMIUM, DUST AND FUME-AIR:CA LOWEST FEASIBLE CONC.
NIOSH* DHHS #92-100,1992
NOHS 1974: HZD 83628; NIS 29; TNF 1041; NOS 41; TNE 19293
NOES 1983: HZD 83628; NIS 32; TNF 1625; NOS 38; TNE 42562; TFE 16685
EPA GENETOX PROGRAM 1988, POSITIVE: CARCINOGENICITY-MOUSE/RAT
EPA GENETOX PROGRAM 1988, POSITIVE: IN VITRO CYTOGENETICS-HUMAN
LYMPHOCYTE
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JANUARY 2001
NTP 9TH REPORT ON CARCINOGENS, 2000:KNOWN TO BE HUMAN CARCINOGEN
U.S. INFORMATION
THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.
CALIFORNIA PROPOSITION 65:
THIS PRODUCT IS OR CONTAINS CHEMICAL(S) KNOWN TO THE STATE OF
CALIFORNIA TO CAUSE CANCER.
THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.
SECTION 16. - - - - - - - - - OTHER INFORMATION- - - - - - - - - - -
THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO
BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA, ALDRICH,
FLUKA SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING
OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR
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APPENDIX B: SIMS ASCII File

IMS   CAMECA
****
****

DEPTH   PROFILE   :   0711010
                                 1.dp

****
****

DEF   ANAL: DEF.   ANALYS
                                 IS

Date	:	07.11.01	Time	:	10:17		
User	name	:	PRINCE				
Sample	name	:	08C				
Sample	stage	position	:	X =	8044 um	Y =	-6998 um
Total	acq.	time	:	2992 s			
Beam	blanking	:	N				
Ref.	signal	:	N				
Auto	HV	cal.	:	N			
Auto	mass	cal.	:	N			
Pre	sputtering	:	N				

MC: MEASUREMENT
           CONDITIONS

133Cs	132.905	FC	wt	1.054 s	ct	1 s	offset	0 V
133Cs 16O	148.9	EM	wt	0.252 s	ct	1 s	offset	0 V
133Cs 28Si	160.882	EM	wt	0.209 s	ct	1 s	offset	0 V
133Cs 32S	164.877	EM	wt	0.136 s	ct	1 s	offset	0 V
133Cs 75As	207.827	EM	wt	0.457 s	ct	1 s	offset	0 V
133Cs 114Cd	246.809	EM	wt	0.394 s	ct	1 s	offset	0 V
133Cs 115In	247.809	EM	wt	0.107 s	ct	1 s	offset	0 V

AP: ANALYTICAL
           PARAMETERS.
           1-   PRIMARY

Ion	:	Cs+		
HV	:	1.06 kV		
Arc	current	:	1.34 mA	
Primary	current	(init.)	:	1.97 nA
Primary	current	(final)	:	2.01 nA
Raster	Size	:	250 um	
Primary	Beam	diameter	:	15 um
MR	Aperture	:	2000	
L4	Aperture	:	750	
Duo	pressure	:		

           2-   SECOND
                      ARY

HV	Sample	:	8.61 kV
Trans	Lens	:	250 um

ESA	inner	:		-557.6 V			
ESA	outer	:		502.9 V			
Slit	entrance	width	:	0 (au)			
Slit	exit	width	:	0 (au)			
Energy	slit	width	:	120			
DTOS	X	:	100 %				
DTOS	Y	:	0 %				
SII	X	:	0 %				
SII	Y	:	0 %				
Mass	reso	:	300				
Contrast	Aperture	:	400				
Field	Aperture	:	400				
Analysis	chamber	pressure:					

3-   DETECTOR PARAMETERS

EM	Yield	:	95 %		
EM	Dead	Time	:25	ns	
EM	Background	:	1.00E-01 c/s		
FC	Background	:	300000 c/s		
EM->FC	Threshold	:	800000 c/s		
FC->EM	Threshold	:	1100000 c/s		

ELEMENT 133Cs		ELEMENT 133Cs 16O		ELEMENT 133Cs 75As		ELEMENT 133Cs 115In	
59 points		59 points		59 points		59 points	
[s]	[c/s]	[s]	[c/s]	[s]	[c/s]	[s]	[c/s]
2.08E+00	2.20E+06	3.34E+00	2.15E+04	7.17E+00	2.60E+02	9.70E+00	1.11E+02
1.18E+01	2.33E+07	1.30E+01	3.46E+04	1.69E+01	1.50E+02	1.94E+01	6.77E+01
2.15E+01	3.76E+07	2.27E+01	3.38E+04	2.66E+01	1.13E+02	2.91E+01	8.26E+01
3.12E+01	4.77E+07	3.24E+01	3.32E+04	3.63E+01	9.21E+01	3.88E+01	6.77E+01
4.09E+01	5.50E+07	4.22E+01	3.16E+04	4.60E+01	6.35E+01	4.85E+01	7.62E+01
5.06E+01	5.97E+07	5.19E+01	3.13E+04	5.57E+01	6.56E+01	5.82E+01	7.41E+01
6.03E+01	6.25E+07	6.16E+01	3.05E+04	6.54E+01	5.40E+01	6.79E+01	7.41E+01
7.00E+01	6.46E+07	7.13E+01	3.00E+04	7.51E+01	4.23E+01	7.76E+01	6.56E+01
7.97E+01	6.60E+07	8.10E+01	2.94E+04	8.48E+01	3.59E+01	8.73E+01	5.08E+01
8.94E+01	6.71E+07	9.07E+01	2.89E+04	9.45E+01	4.23E+01	9.70E+01	6.35E+01
9.91E+01	6.77E+07	1.00E+02	2.86E+04	1.04E+02	4.23E+01	1.07E+02	6.88E+01
1.09E+02	6.85E+07	1.10E+02	2.78E+04	1.14E+02	3.81E+01	1.16E+02	8.36E+01
1.19E+02	6.91E+07	1.20E+02	2.76E-04	1.24E+02	5.50E+01	1.26E+02	7.73E+01
1.28E+02	6.97E+07	1.29E+02	2.72E+04	1.33E+02	4.87E+01	1.36E+02	7.41E+01
1.38E+02	7.01E+07	1.39E+02	2.64E+04	1.43E+02	4.97E+01	1.46E+02	7.20E+01
1.48E+02	7.04E+07	1.49E+02	2.63E+04	1.53E+02	4.12E+01	1.55E+02	7.09E+01
1.57E+02	7.07E+07	1.59E+02	2.55E+04	1.62E+02	4.12E+01	1.65E+02	7.62E+01
1.67E+02	7.10E+07	1.68E+02	2.53E+04	1.72E+02	4.76E+01	1.75E+02	8.79E+01
1.77E+02	7.13E+07	1.78E+02	2.47E+04	1.82E+02	4.44E+01	1.84E+02	9.10E+01
1.86E+02	7.15E+07	1.88E+02	2.47E+04	1.92E+02	4.87E+01	1.94E+02	8.89E+01
1.96E+02	7.18E+07	1.97E+02	2.42E+04	2.01E+02	5.61E+01	2.04E+02	8.04E+01
2.06E+02	7.19E+07	2.07E+02	2.36E+04	2.11E+02	4.02E+01	2.14E+02	9.63E+01
2.16E+02	7.22E+07	2.17E+02	2.35E+04	2.21E+02	4.76E+01	2.23E+02	1.14E+02
2.25E+02	7.20E+07	2.27E+02	2.30E+04	2.30E+02	4.12E+01	2.33E+02	1.31E+02
2.35E+02	7.20E+07	2.36E+02	2.27E+04	2.40E+02	4.76E+01	2.43E+02	1.16E+02
2.45E+02	7.21E+07	2.46E+02	2.21E+04	2.50E+02	4.44E+01	2.52E+02	1.32E+02
2.54E+02	7.22E+07	2.56E+02	2.22E+04	2.59E+02	4.02E+01	2.62E+02	1.42E+02
2.64E+02	7.21E+07	2.65E+02	2.19E+04	2.69E+02	4.76E+01	2.72E+02	1.44E+02
2.74E+02	7.22E+07	2.75E+02	2.15E+04	2.79E+02	4.97E+01	2.81E+02	1.56E+02

2.84E+02	7.21E+07	2.85E+02	2.12E+04	2.89E+02	5.61E+01	2.91E+02	1.76E+02
2.93E+02	7.21E+07	2.94E+02	2.11E+04	2.98E+02	5.29E+01	3.01E+02	1.99E+02
3.03E+02	7.20E+07	3.04E+02	2.10E+04	3.08E+02	5.82E+01	3.11E+02	2.21E+02
3.13E+02	7.19E+07	3.14E+02	2.06E+04	3.18E+02	5.61E+01	3.20E+02	2.62E+02
3.22E+02	7.17E+07	3.24E+02	2.05E+04	3.27E+02	6.14E+01	3.30E+02	2.80E+02
3.32E+02	7.16E+07	3.33E+02	2.01E+04	3.37E+02	4.87E+01	3.40E+02	3.05E+02
3.42E+02	7.14E+07	3.43E+02	1.97E+04	3.47E+02	4.12E+01	3.49E+02	2.95E+02
3.51E+02	7.12E+07	3.53E+02	1.97E+04	3.57E+02	4.87E+01	3.59E+02	3.14E+02
3.61E+02	7.11E+07	3.62E+02	1.97E+04	3.66E+02	5.93E+01	3.69E+02	3.34E+02
3.71E+02	7.07E+07	3.72E+02	1.96E+04	3.76E+02	4.97E+01	3.78E+02	3.79E+02
3.81E+02	7.03E+07	3.82E+02	1.88E+04	3.86E+02	5.18E+01	3.88E+02	4.44E+02
3.90E+02	7.00E+07	3.92E+02	1.88E+04	3.95E+02	5.61E+01	3.98E+02	4.34E+02
4.00E+02	6.97E+07	4.01E+02	1.84E+04	4.05E+02	5.61E+01	4.08E+02	4.31E+02
4.10E+02	6.93E+07	4.11E+02	1.83E+04	4.15E+02	5.50E+01	4.17E+02	5.24E+02
4.19E+02	6.87E+07	4.21E+02	1.79E+04	4.24E+02	5.71E+01	4.27E+02	5.13E+02
4.29E+02	6.82E+07	4.30E+02	1.75E+04	4.34E+02	4.55E+01	4.37E+02	4.99E+02
4.39E+02	6.74E+07	4.40E+02	1.73E+04	4.44E+02	5.08E+01	4.46E+02	5.90E+02
4.48E+02	6.67E+07	4.50E+02	1.71E+04	4.54E+02	4.87E+01	4.56E+02	5.84E+02
4.58E+02	6.58E+07	4.59E+02	1.65E+04	4.63E+02	6.03E+01	4.66E+02	6.31E+02
4.68E+02	6.47E+07	4.69E+02	1.61E+04	4.73E+02	5.18E+01	4.76E+02	7.15E+02
4.78E+02	6.35E+07	4.79E+02	1.56E+04	4.83E+02	6.03E+01	4.85E+02	7.06E+02
4.87E+02	6.21E+07	4.89E+02	1.49E+04	4.92E+02	4.97E+01	4.95E+02	7.26E+02
4.97E+02	6.08E+07	4.98E+02	1.42E+04	5.02E+02	6.56E+01	5.05E+02	6.84E+02
5.07E+02	5.94E+07	5.08E+02	1.40E+04	5.12E+02	4.34E+01	5.14E+02	7.76E+02
5.16E+02	5.78E+07	5.18E+02	1.32E+04	5.22E+02	5.08E+01	5.24E+02	7.86E+02
5.26E+02	5.57E+07	5.27E+02	1.26E+04	5.31E+02	4.44E+01	5.34E+02	8.14E+02
5.36E+02	5.25E+07	5.37E+02	1.15E+04	5.41E+02	4.76E+01	5.43E+02	7.50E+02
5.46E+02	4.61E+07	5.47E+02	9.63E+03	5.51E+02	4.34E+01	5.53E+02	6.03E+02
5.55E+02	3.13E+07	5.56E+02	5.74E+03	5.60E+02	2.85E+01	5.63E+02	1.56E+02
5.65E+02	3.63E+06	5.66E+02	5.03E+02	5.70E+02	9.55E-01	5.73E+02	4.13E+00

ELEMENT 133Cs 28Si		ELEMENT 133Cs 32S		ELEMENT 133Cs 114Cd	
59 points		59 points		59 points	
[s]	[c/s]	[s]	[c/s]	[s]	[c/s]
4.56E+00	8.62E+02	5.70E+00	4.84E+04	8.58E+00	3.13E+04
1.43E+01	6.15E+02	1.54E+01	6.70E+04	1.83E+01	5.97E+04
2.40E+01	3.45E+02	2.51E+01	7.04E+04	2.80E+01	7.32E+04
3.37E+01	2.89E+02	3.48E+01	6.96E+04	3.77E+01	7.99E+04
4.34E+01	2.73E+02	4.45E+01	6.83E+04	4.74E+01	8.36E+04
5.31E+01	2.82E+02	5.42E+01	6.57E+04	5.71E+01	8.54E+04
6.28E+01	3.09E+02	6.39E+01	6.49E+04	6.68E+01	8.61E+04
7.25E+01	3.24E+02	7.36E+01	6.41E+04	7.65E+01	8.65E+04
8.22E+01	3.01E+02	8.33E+01	6.38E+04	8.62E+01	8.73E+04
9.19E+01	3.46E+02	9.30E+01	6.26E+04	9.59E+01	8.75E+04
1.02E+02	3.67E+02	1.03E+02	6.16E+04	1.06E+02	8.80E+04
1.11E+02	3.46E+02	1.12E+02	6.15E+04	1.15E+02	8.88E+04
1.21E+02	3.56E+02	1.22E+02	6.04E+04	1.25E+02	8.86E+04
1.31E+02	3.83E+02	1.32E+02	6.06E+04	1.35E+02	8.92E+04
1.40E+02	4.09E+02	1.42E+02	6.05E+04	1.44E+02	8.93E+04
1.50E+02	3.87E+02	1.51E+02	5.99E+04	1.54E+02	9.02E+04
1.60E+02	4.03E+02	1.61E+02	5.96E+04	1.64E+02	8.98E+04
1.70E+02	3.92E+02	1.71E+02	5.98E+04	1.74E+02	9.02E+04
1.79E+02	4.61E+02	1.80E+02	5.91E+04	1.83E+02	9.06E+04
1.89E+02	4.56E+02	1.90E+02	5.92E+04	1.93E+02	9.08E+04
1.99E+02	4.95E+02	2.00E+02	5.87E+04	2.03E+02	9.06E+04
2.08E+02	4.51E+02	2.09E+02	5.83E+04	2.12E+02	9.05E+04

2.18E+02	4.93E+02	2.19E+02	5.84E+04	2.22E+02	9.04E+04
2.28E+02	5.57E+02	2.29E+02	5.79E+04	2.32E+02	9.03E+04
2.37E+02	5.16E+02	2.39E+02	5.78E+04	2.41E+02	9.05E+04
2.47E+02	5.56E+02	2.48E+02	5.82E+04	2.51E+02	9.09E+04
2.57E+02	5.88E+02	2.58E+02	5.77E+04	2.61E+02	9.08E+04
2.67E+02	6.09E+02	2.68E+02	5.79E+04	2.71E+02	8.98E+04
2.76E+02	5.78E+02	2.77E+02	5.73E+04	2.80E+02	9.01E+04
2.86E+02	6.41E+02	2.87E+02	5.76E+04	2.90E+02	9.07E+04
2.96E+02	6.16E+02	2.97E+02	5.73E+04	3.00E+02	9.01E+04
3.05E+02	6.84E+02	3.07E+02	5.74E+04	3.09E+02	8.97E+04
3.15E+02	6.61E+02	3.16E+02	5.75E+04	3.19E+02	8.93E+04
3.25E+02	6.91E+02	3.26E+02	5.71E+04	3.29E+02	8.87E+04
3.35E+02	6.80E+02	3.36E+02	5.70E+04	3.39E+02	8.82E+04
3.44E+02	6.80E+02	3.45E+02	5.72E+04	3.48E+02	8.84E+04
3.54E+02	7.49E+02	3.55E+02	5.64E+04	3.58E+02	8.78E+04
3.64E+02	7.64E+02	3.65E+02	5.66E+04	3.68E+02	8.73E+04
3.73E+02	7.70E+02	3.74E+02	5.59E+04	3.77E+02	8.62E+04
3.83E+02	8.41E+02	3.84E+02	5.57E+04	3.87E+02	8.58E+04
3.93E+02	8.53E+02	3.94E+02	5.55E+04	3.97E+02	8.51E+04
4.02E+02	9.46E+02	4.04E+02	5.53E+04	4.06E+02	8.47E+04
4.12E+02	8.36E+02	4.13E+02	5.45E+04	4.16E+02	8.35E+04
4.22E+02	9.46E+02	4.23E+02	5.42E+04	4.26E+02	8.23E+04
4.32E+02	9.60E+02	4.33E+02	5.30E+04	4.36E+02	8.04E+04
4.41E+02	9.61E+02	4.42E+02	5.25E+04	4.45E+02	7.97E+04
4.51E+02	1.00E+03	4.52E+02	5.14E+04	4.55E+02	7.82E+04
4.61E+02	1.08E+03	4.62E+02	5.01E+04	4.65E+02	7.68E+04
4.70E+02	1.07E+03	4.72E+02	4.94E+04	4.74E+02	7.42E+04
4.80E+02	1.10E+03	4.81E+02	4.79E+04	4.84E+02	7.20E+04
4.90E+02	1.13E+03	4.91E+02	4.62E+04	4.94E+02	6.97E+04
4.99E+02	1.18E+03	5.01E+02	4.46E+04	5.04E+02	6.74E+04
5.09E+02	1.16E+03	5.10E+02	4.28E+04	5.13E+02	6.46E+04
5.19E+02	1.34E+03	5.20E+02	4.07E+04	5.23E+02	6.16E+04
5.29E+02	1.26E+03	5.30E+02	3.87E+04	5.33E+02	5.78E+04
5.38E+02	1.27E+03	5.39E+02	3.53E+04	5.42E+02	5.25E+04
5.48E+02	1.13E+03	5.49E+02	2.86E+04	5.52E+02	4.12E+04
5.58E+02	7.01E+02	5.59E+02	1.51E+04	5.62E+02	1.50E+04
5.67E+02	3.59E+01	5.69E+02	5.68E+02	5.71E+02	2.92E+02

APPENDIX C: ANSTO SIMS SAMPLE PREPARATION

Sample Requirements for the ANSTO Cameca ims 5f SIMS.

Introduction

The Cameca ims5F Secondary Ion Mass Spectrometer (SIMS) is a high-precision instrument that operates under an Ultra-High Vacuum (UHV) environment. To preserve this environment, certain precautions need to be taken in the preparation of samples to analyse in the machine. This document outlines the requirements for preparing suitable samples for SIMS analysis in the Cameca ims5f at ANSTO.

There is a fair amount of information and several requirements here, but they can effectively be summarised as:

The sample must be flat, hard, dry, clean, smaller than 25mm in diameter and less than 10mm thick.
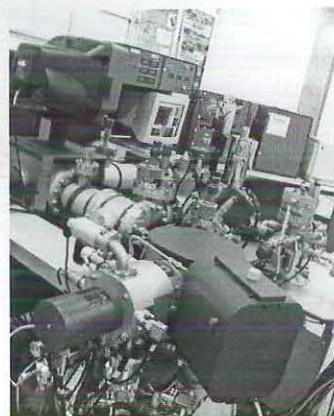
Sample Handling

Samples must not be handled directly. Clean gloves or tools such as clean tweezers should be used to handle samples at all times to prevent sample contamination, which leads to vacuum problems (outgassing, see below) and high background signals. Fingerprints outgas and are not SIMS-compatible! They must be removed with a suitable solvent such as ethanol or deionised water before analysis.

Samples must not be contaminated with material such as oil or grease. If a sample is contaminated, it should be washed with a suitable solvent such as ethanol and/or deionised water, preferably in an ultrasonic bath.

Sample Dimensions

Minimum:

> length × width: 3×1 mm
>
> Thickness: 1 mm, dependent on sample strength

Note a 3×1 mm sample is not desirable. Sample fragility is important as the sample may be subjected to various stresses when fixed in a SIMS sample holder. Small samples can be analysed if they are mounted, for example in resin or on a larger material (See below).

Maximum:

> Circular Sample: 2.5 cm diameter
>
> Square Sample: 1.79 cm × 1.79 cm
>
> Thickness: 1 cm

Sample Holder Schematics

A set of sample holder schematics is below showing the available sample holder faceplates. Also included are actual photos of the 18-hole sample holder.

| 1 Hole Holder | 3 Hole Holder | 9 Hole Holder | 14 Hole Holder | 18 Hole Holder |
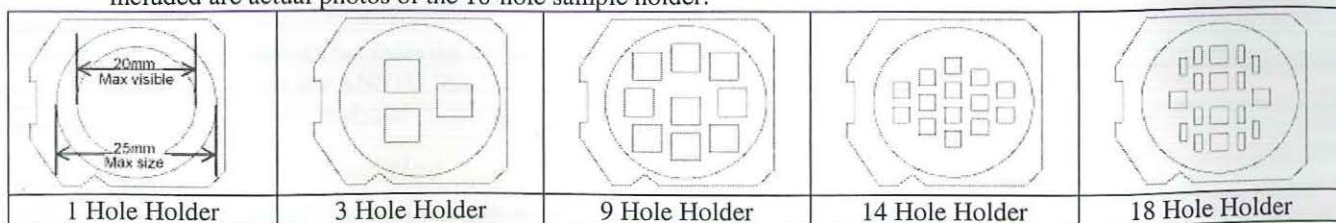
Figure 1: Schematics of available holder faceplates.

	Picture of 18 hole sample holder, rear side. Sample holders are available with various face plate patterns.
	Picture of sample holder, front side. Samples must lie flush with this face for analysis.

Figure 2
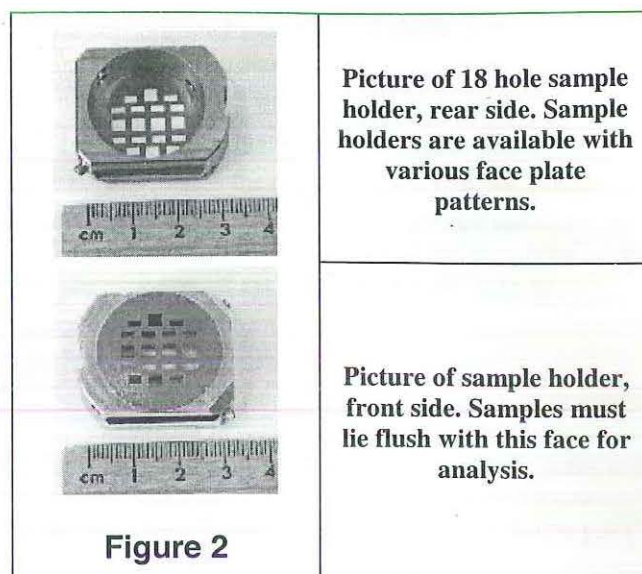
Vacuum Requirements

A sample and mounting material able to withstand ultra-high vacuum is required ie solid, non-volatile and non-porous.

Preferred Sample Properties

Properties that assist with sample analysis and reliability of results are:

- A flat, polished analysis surface.
- Electrically conductive sample material.
- Homogeneous material. If the sample is heterogeneous, a map or photo of the surface to locate the analysis sites is very useful.
- Symmetrical samples.
- A flat back, alternatively a cylindrical shape not less than 1.5cm in diameter (for fixing in the SIMS sample holder).

Sample Acceptability

Acceptable samples

Samples which are not necessarily of the ideal dimensions or qualities but which possess a flat analysis surface may still be acceptable without requiring sample mounting. All samples must fit into one of the sample holders that are shown in Figure 1 and Figure 2. For example, the following samples could still be accepted as-is.

1. A square metal plate, 1.5cm × 1.5cm × 2mm (L × W × H)
2. Semiconductor wafer material, such as Si or GaAs.
3. Irregularly shaped material less than 1.5cm × 1.5cm × 5mm (L × W × H) that has a smooth, flat analysis surface larger than the minimum specifications above.
4. Cleaved or polished minerals.
5. Materials mounted in resin with the analysis surface exposed.

For samples that do not meet the above specifications, for example powders, soils and biologically based samples, contact the ANSTO SIMS staff for advice and assistance on the preparation and mounting of samples for SIMS analysis.

Undesirable Qualities

If present these sample qualities will prevent a proper analysis being performed.
- Curled edges that protrude from the analysis surface (eg a piece of metal cut with tin snips).

- Sample analysis surfaces contaminated and/or buried under resin (see Mounting samples In Resin, below) or other inappropriate foreign material.
- Samples "dirty" with fingerprints, oil, power, cleaning paste, polishing paste, etc.
- Damp, wet or uncured (ie samples only put in resin a couple of hours ago/the night before) samples.
- Samples marked with ink pens (unless the ink is encapsulated, for example in resin).
- Samples compatible with SEMs, electron microprobes, etc. are not necessarily SIMS compatible. Check with a member of the ANSTO SIMS staff beforehand for advice. Common "sticky-tape" is not SIMS-compatible, although special vacuum "sticky-tape" may be.

Sample Outgassing

All samples outgas (sometimes for days) so consult the SIMS staff about this possibility well before scheduled analysis time. Some examples of problem samples for outgassing include cement material, oil shales, shells, resin-mounted material. A vacuum pumping station is available in the SIMS laboratory for the outgassing of samples prior to analysis. If there is any question of outgassing, please contact a SIMS team member to evaluate the necessity of outgassing in the pumping station prior to analysis.

Non-conductive Samples

Samples which are non-conductive lead to analysis problems in the SIMS. Examples include some minerals such as sphalerite, biological material, glass, plastics and resin. Samples which do not conduct electricity have to be either charge-compensated during analysis (problematic) or coated with a conductive layer (eg Gold) prior to analysis. Gold coating of non-conductive samples can be performed in the SIMS laboratory. Charge compensation is possible, but time-consuming and not always reliable. Samples coated with carbon (eg for SEM) are also acceptable, however it should be noted that analysis for carbon, or species with masses which may have carbon-related interferences (C_2, CH_2, etc), will be somewhat difficult due to the overwhelming background.

Mounting samples

On or in another material

Samples that are too small or irregular may be mounted on another piece of material, such as a piece of flat metal, a SEM sample stub with pin removed or other suitable material. If done so, the sample should be fixed with silver paint, which will provide a good electrical contact. If the sample is mounted on a non-conductive material such as glass, then further steps such as gold coating may need to be taken to ensure a good electrical ground of the sample is made.

In Resin

Samples that do not readily present their surface for analysis, for example mineral grains and biological material, may require sample mounting in a vacuum-compatible resin. Samples which have analysis surfaces smaller than $3 \times 1mm$ will almost certainly require mounting in a resin to be compatible with the SIMS sample holders. Samples should be mounted with the analysis surface flush with the top of the resin. Refer to Figure 3.
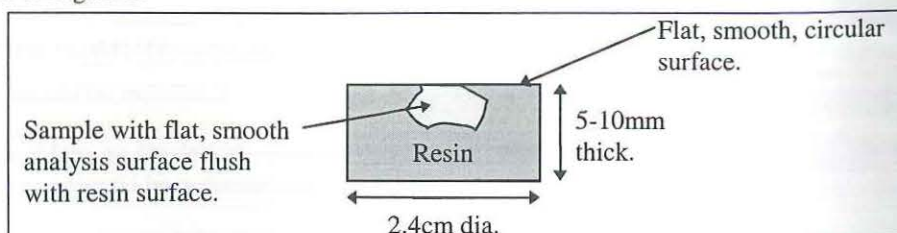
**Figure 3: Example of a sample mounted in cylindrical resin.
Side-on view.**

Types of resin to use

The following resins have been found to perform acceptably for SIMS analysis when mixed properly. There may be others that are also acceptable. Once set, these resins may require a couple of days of outgassing in a vacuum chamber. All resins when ordered as a kit should come with the appropriate hardener and instructions on correct mixing procedures.

Resin Name	Company	Contact Address	Extra Info
EPIREZ 133	Epirez Construction Products	2 Seville Street, Villawood NSW 2163 Australia ph: +61-2-9726-8899	
Daystar Resin LC3600	Daystar	396 Princes Hwy, Rockdale NSW 2216 Australia ph: +61-2-9567-3328	
Epoxy Resin QC (Quick Cure)	Leco Aust. Pty. Ltd.	4/10 Salisbury Rd, Castle Hill NSW 2154 Australia ph: +61-2-9894-5955	5:1 (resin:hardener) Small Kit 811-563-130: $88.75
EPO-THIN	Selby-Biolab	Unit 5/43-51 College St, Gladesville NSW 2111 ph: 13 2991	Thin, suitable for porous samples, filling small voids and holes.

Avoid getting resin onto the analysis face of the sample. Filling pores or holes in the analysis face (especially when using with EPO_THIN) may result in analysis results reflecting the resin rather than your sample.

An "Ideal" sample

The "ideal" vacuum-compatible sample would be a solid cylindrical disc 2.4cm in diameter and 5mm thick, electrically conductive, non-porous/impermeable and homogeneous with flat, polished surfaces. Refer to Figure 4.
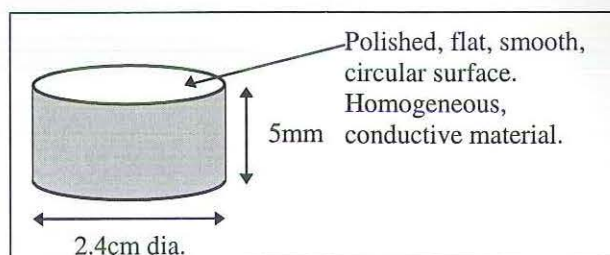
Figure 4: The "ideal" sample.

Sample Identification

Samples should be individually identifiable, preferably with distinctive markings or labels placed on the sample, eg by using a diamond scribe. Do not use a standard ink pen (vacuum compatibility problems). If this is a problem, eg for delicate samples such as thin wafers, and small pieces of irregular-shaped material, they should be encapsulated individually with the identification clearly marked on the capsule.

Sample Submission

Samples may be:
1. Submitted in person.
2. Submitted by courier.
3. Sent by mail in a padded envelope or box.

Samples submitted by mail or courier should arrive at least 5 working days before the scheduled analysis time. This is especially important for samples that need to be placed in the vacuum pumping station for outgassing prior to analysis.

If samples are to be submitted by courier or mail without the researcher being present during analysis, they should be accompanied by the following information:

- Analysis type (eg depth profile or imaging)

- Species to be analysed for (if necessary)

- Analysis conditions if known. Consult SIMS staff- primary beam type, current, raster size, max/min depth required.

- Sample name, composition, type, structure, size, placement, position (if not obvious), **side or face to be analysed** and anything else considered necessary to identify the sample and perform the analysis required. Diagrams are most helpful.

If there are any further questions, or something is not clear, please contact one of the SIMS team members for more details.

Contact Details

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	ANSTO	
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Email:	kathryn.prince@ansto.gov.au	
Last update:	10/14/02	

APPENDIX D: X-Ray Emission Lines

K-level and *L*-level emission lines in KeV

No.	Element	Ka1	Ka2	Kb1	La1	La2	Lb1
3	Li	0.0543					
4	Be	0.1085					
5	B	0.1833					
6	C	0.277					
7	N	0.3924					
8	O	0.5249					
9	F	0.6768					
10	Ne	0.8486	0.8486				
11	Na	1.04098	1.04098	1.0711			
12	Mg	1.25360	1.25360	1.3022			
13	Al	1.48670	1.48627	1.55745			
14	Si	1.73998	1.73938	1.83594			
15	P	2.0137	2.0127	2.1391			
16	S	2.30784	2.30664	2.46404			
17	Cl	2.62239	2.62078	2.8156			
18	Ar	2.95770	2.95563	3.1905			
19	K	3.3138	3.3111	3.5896			
20	Ca	3.69168	3.68809	4.0127	0.3413	0.3413	0.3449
21	Sc	4.0906	4.0861	4.4605	0.3954	0.3954	0.3996
22	Ti	4.51084	4.50486	4.93181	0.4522	0.4522	0.4584
23	V	4.95220	4.94464	5.42729	0.5113	0.5113	0.5192
24	Cr	5.41472	5.405509	5.94671	0.5728	0.5728	0.5828
25	Mn	5.89875	5.88765	6.49045	0.6374	0.6374	0.6488
26	Fe	6.40384	6.39084	7.05798	0.7050	0.7050	0.7185
27	Co	6.93032	6.91530	7.64943	0.7762	0.7762	0.7914
28	Ni	7.47815	7.46089	8.26466	0.8515	0.8515	0.8688
29	Cu	8.04778	8.02783	8.90529	0.9297	0.9297	0.9498
30	Zn	8.63886	8.61578	9.5720	1.0117	1.0117	1.0347
31	Ga	9.25174	9.22482	10.2642	1.09792	1.09792	1.1248
32	Ge	9.88642	9.85532	10.9821	1.18800	1.18800	1.2185
33	As	10.54372	10.50799	11.7262	1.2820	1.2820	1.3170
34	Se	11.2224	11.1814	12.4959	1.37910	1.37910	1.4192
35	Br	11.9242	11.8776	13.2914	1.48043	1.48043	1.5259
36	Kr	12.649	12.598	14.112	1.5860	1.5860	1.6366
37	Rb	13.3953	13.3358	14.9613	1.69413	1.69256	1.7521
38	Sr	14.1650	14.0979	15.8357	1.80656	1.80474	1.8717
39	Y	14.9584	14.8829	16.7378	1.92256	1.92047	1.9958
40	Zr	15.7751	15.6909	17.6678	2.04236	2.0399	2.1244
41	Nb	16.6151	16.5210	18.6225	2.16589	2.1630	2.2574
42	Mo	17.47934	17.3743	19.6083	2.29316	2.28985	2.3948
43	Tc	18.3671	18.2508	20.619	2.4240	-	2.5368
44	Ru	19.2792	19.1504	21.6568	2.55855	2.55431	2.6832
45	Rh	20.2161	20.0737	22.7236	2.69674	2.69205	2.8344
46	Pd	21.1771	21.0201	23.8187	2.83861	2.83325	2.9902
47	Ag	22.16292	21.9903	24.9424	2.98431	2.97821	3.1509
48	Cd	23.1736	22.9841	26.0955	3.13373	3.12691	3.3165
49	In	24.2097	24.0020	27.2759	3.28694	3.27929	3.4872
50	Sn	25.2713	25.0440	28.4860	3.44398	3.43542	3.6628
51	Sb	26.3591	26.1108	29.7256	3.60472	3.59532	3.8435
52	Te	27.4723	27.2017	30.9957	3.76933	3.7588	4.0295
53	I	28.6120	28.3172	32.2947	3.93765	3.92604	4.2207
54	Xe	29.779	29.458	33.624	4.1099	-	-
55	Cs	30.9728	30.6251	34.9869	4.2865	4.2722	4.6198

56	Ba	32.1936	31.8171	36.3782	4.46626	4.45090	4.8275
57	La	33.4418	33.0341	37.8010	4.65097	4.63423	5.0421
58	Ce	34.7197	34.2789	39.2573	4.8402	4.8230	5.2622
59	Pr	36.0263	35.5502	40.7482	5.0337	5.0135	5.4889
60	Nd	37.3610	36.8474	42.2713	5.2304	5.2077	5.7216
61	Pm	38.7247	38.1712	43.826	5.4325	5.4078	5.961
62	Sm	40.1181	39.5224	45.413	5.6361	5.6090	6.2051
63	Eu	41.5422	40.9019	47.0379	5.8457	5.8166	6.4564
64	Gd	42.9962	42.3089	48.697	6.0572	6.0250	6.7132
65	Tb	44.4816	43.7441	50.382	6.2728	6.2380	6.978
66	Dy	45.9984	45.2078	52.119	6.4952	6.4577	7.2477
67	Ho	47.5467	46.6997	53.877	6.7198	6.6795	7.5253
68	Er	49.1277	48.2211	55.681	6.9487	6.9050	7.8109
69	Tm	50.7416	49.7726	57.517	7.1799	7.1331	8.101
70	Yb	52.3889	51.3540	59.37	7.4156	7.3673	8.4018
71	Lu	54.0698	52.9650	61.283	7.6555	7.6049	8.7090
72	Hf	55.7902	54.6114	63.234	7.8990	7.8446	9.0227
73	Ta	57.532	56.277	65.223	8.1461	8.0879	9.3431
74	W	59.31824	57.9817	67.2443	8.3976	8.3352	9.6723
75	Re	61.1403	59.7179	69.310	8.6525	8.5862	10.010
76	Os	63.0005	61.4867	71.413	8.9117	8.8410	10.355
77	Ir	64.8956	63.2867	73.5608	9.1751	9.0995	10.708
78	Pt	66.832	65.112	75.748	9.4423	9.3618	11.070
79	Au	68.8037	66.9895	77.984	9.7133	9.6280	11.442
80	Hg	70.819	68.895	80.253	9.9888	9.8976	11.822
81	Tl	72.8715	70.8319	82.576	10.2685	10.1728	12.213
82	Pb	74.9694	72.8042	84.936	10.5515	10.4495	12.613
83	Bi	77.1079	74.8148	87.343	10.8388	10.73091	13.023
84	Po	79.290	76.862	89.80	11.1308	11.0158	13.447
85	At	81.52	78.95	92.30	11.4268	11.3048	13.876
86	Rn	83.78	81.07	94.87	11.7270	11.5979	14.316
87	Fr	86.10	83.23	97.47	12.0313	11.8950	14.770
88	Ra	88.47	85.43	100.13	12.3397	12.1962	15.235
89	Ac	90.884	87.67	102.85	12.6520	12.5008	15.713
90	Th	93.350	89.953	105.609	12.9687	12.8096	16.202
91	Pa	95.868	92.287	108.427	13.2907	13.1222	16.702
92	U	98.439	94.665	111.300	13.6147	13.4388	17.220
93	Np	-	-	-	13.9441	13.7597	17.750
94	Pu	-	-	-	14.2786	14.0842	18.293
95	Am	-	-	-	14.6172	14.4119	18.852

Values are from J. A. Bearden, "X-Ray Wavelengths", *Review of Modern Physics*, (January 1967) pp. 86-99, unless otherwise noted.

APPENDIX E: Acronyms

CBD   Chemical Bath Deposition

SIMS   Secondary Ion Mass Spectroscopy

ESEM   Environmental Scanning Electron Microscope

CCI   Charge Contrast Imaging

PIXE   Proton Induced X-ray Emission

AINSE   Australian Institute of Nuclear Science and Engineering

ANSTO   Australian Nuclear Science and Technology Organisation

MSDS   Materials Safety Data Sheet

TFT   Thin Film Transistor

TCO   Transparent Conducting Oxide

EDAX   Energy Dispersive Analysis of X-rays

WACM   Western Australian Centre for Microscopy

PLA   Pressure Limiting Aperture

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