Zinc phthalocyanine on aluminium dosed complex metallic alloys.

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Declaration

I hereby declare that this thesis is my own work and effort and that it has not been submitted anywhere for any award. Where other sources of information have been used, they have been acknowledged.

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Abstract

The adsorption and diffusion of zinc phthalocyanine on a Al_9Co_2 (001) surface are studied using Scanning Tunnelling Microscopy in Ultra High Vacuum conditions to determine adsorption sites on the substrate and to analyse the molecular diffusion of the ZnPc across the surface so that we have a more complete picture of their behaviour. It was shown that there were four different adsorption sites on the surface which differ electronically. Analysis of the diffusion of the ZnPc adatoms at three different temperatures, room temperature (RT), 312K and 350K, showed that, the percentage of moving molecules increased with increasing temperature and the average ratio of the number of moving molecules to the number of stationary molecules also increased with increasing temperature. This told us that both the number of diffusing molecules and the jump rate of the molecules increased with temperature.

1 Introduction

Surface Physics is the study of physical and chemical phenomena that occur at the interface of two phases [1]. The surface of a material cannot be reduced to the concepts of bulk solid state physics as any contact between two different phases leads to the alteration of their properties at the interface, from the respective bulk. Atomic level understanding of a surface is necessary as it allows us to characterise surfaces at the atomic level giving us the ability to understand and hence tailor the properties of surfaces. The discipline of Surface Physics has developed massively over recent years and has become an important and influential sector of solid-state physics, especially when considering the output into important fields of application. Surface Physics has contributed to the development of many industrial applications, such as; the deeper understanding of adsorption and reaction mechanisms on catalytically active surfaces (necessary to optimize the reactivity of a surface), in addition to better understanding of corrosion processes on the surface which has led to advancement of surface protection, as corrosion can be controlled by surface modification. Modern semiconductor device technology has also benefited from Surface Physics technologies; with increasing trend to miniaturisation, developments in thin film deposition and preparation techniques has led to new complex multilayer devices and nanostructures [2].

The adsorption and ordering of molecular species at atomically well-defined surfaces is a central topic in surface science, this can be investigated by looking at both the physical properties of thin films and their growth mechanisms [2]. The properties of a thin film are defined by the properties of its two interfaces, the solid – solid interface and its surface. For this project an Aluminium based Complex Metal Alloy (CMA) surface was dosed with Zinc phthalocyanine (ZnPc) with the aims of investigating how the surface is modulated by its complexity - in other words how the introduction of additional atoms into the substrate affects the surface electronically and hence surface adsorption behaviour, and to see if the dopant arrange themselves in a specific way and hence whether it’s possible for the ZnPc molecules to polymerise for functionalisation. The objectives of this project is to analyse adsorption sites on the substrate and to analyse the molecular diffusion of the ZnPc across the surface so that we have a more complete picture of their behaviour.

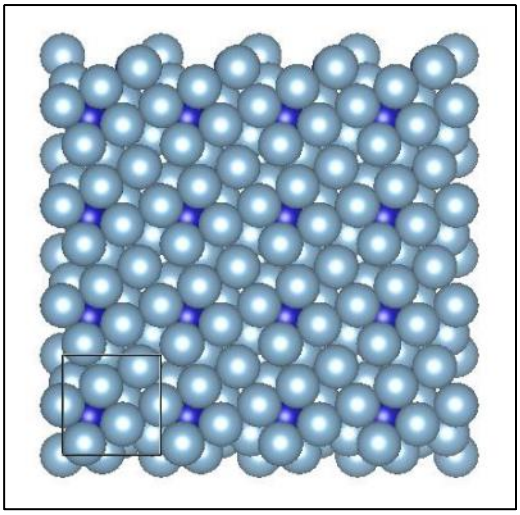

Figure 1 *VESTA model of Al*$_9$*Co*$_2$ *(001) surface.*

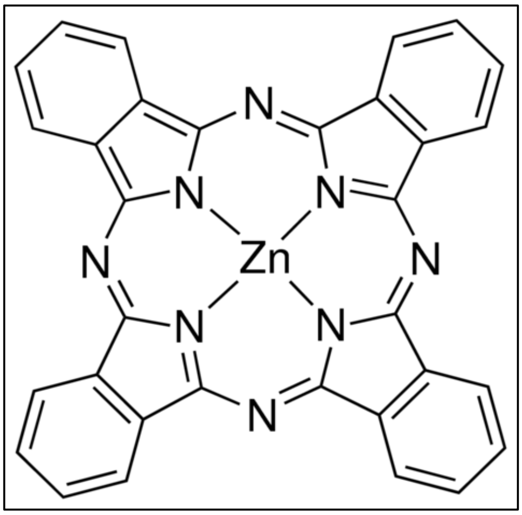

Figure 2 *Image of chemical structure of zinc phthalocyanine molecule.*

Zinc phthalocyanine (ZnPc) is an organic semi-conductor which has been noted for its potential for photovoltaic applications. Organic semi-conductors are used in photovoltaic cells due to their flexibility in varying their electrical and optical properties. ZnPc is an attractive candidate for use in producing solar-cells as it is easily synthesised, non-toxic and phthalocyanine compounds are very durable [3]. Complex Metal Alloys (CMAs) are crystalline compounds characterised by having very large unit cells comprising of up to thousands of atoms, the occurrence of well-defined atomic clusters and the existence of an inherent disorder in the ideal structure [4]. Due to the large unit cells the periodicity of the crystals no longer influence the physical properties of the crystal. The CMA chosen was Aluminium-9 Cobalt-2 (Al_9Co_2), this was due to its aptitude for being used to investigate the structural complexity of an Al based transition metal alloys as it is an intermediate in structural complexity between simple alloy such as B_2AlCo and the AlNiCo quasicrystal [4]. Quasicrystals are CMA's with an infinite unit cell and whose structure is ordered but not periodic.

2 Methodology

The key aspect of surface science experiments is to ensure an atomically clean surface under controlled conditions. Here the methods of achieving and maintaining a clean surface during this project are discussed as well as the methods used to analyse the surface itself.

2.1 UHV Chamber

Ultra High Vacuum (UHV) equipment is required to establish clean conditions for the preparation of a well-defined solid surface and for the performance of experiments on a freshly prepared interface. Conducting experiments in UHV conditions allows us avoid contamination of the surface from ambient gases, maintaining the surface cleanliness over the period of an experiment. In addition to this they help avoid any interference of probes used to scan the surface by the surrounding environment. It is necessary to reach of pressures of $< 10^{-6}$ mbar for a collision free experiment and pressures of $<10^{-9}$ mbar to maintain a clean surface for the duration of the experiment [2].

For this experiment a series of pumps are used to attain pressures of up to 10^{-10} mbar. The first pump is a Rotary pump, these are positive-displacement pumps that consists of variable length, spring tensioned vanes mounted to a rotor that rotates inside of a circular cavity. The vane is pressed against the wall of the chamber when the rotor is driven to rotate by an electric motor, the fact the vanes are tensioned allows them to maintain contact with the wall as the pump rotates. The pump has an inlet to the vacuum system and an outlet to the atmosphere. As the rotor rotates, gas molecules from the chamber enters the cavity via the inlet, and with further rotation the inlet is closed and the gas from the chamber is compressed and forced through the valve in the outlet – resulting in gas being pumped out of the system [6]. With continuous rotations, pressures can reach 10^{-3} mbar. The rotary pump acts as a roughening pump for the next pump which is connected in series; a Turbo-molecular pump. These pumps work on the principle that gas molecules can be given momentum in a desired direction by repeated collision with a moving solid surface. This is achieved by using pairs of angled blades, a quickly rotating rotor blade and a stationary stator blade, inclined in reverse directions mounted in series. Momentum from the rotors is transferred to inlet molecules which are directed toward the outlet, which is connected to the rotary pump [6]. The final pump is an Ion pump, an ion pump ionizes gas within the vessel via an electrical discharge from a strong electrical potential, typically 3–7 keV between an anode and cathode, which hence accelerates the ions to the Titanium cathode, where they are captured or chemisorbed. A magnetic field is also employed as it forces electrons into a helical path, this increases the probability of collision with the inlet gas molecules to form positive ions. Multiple cells are used to enhance pumping. Ion pumps only operate at pressures lower than 10^{-4} mbar which means it’s necessary to ‘rough out the system’ to create an initial vacuum, the rotary and turbo-molecular pumps are used as roughening pumps until a suitable pressure is reached when the ion pump can be used [2].

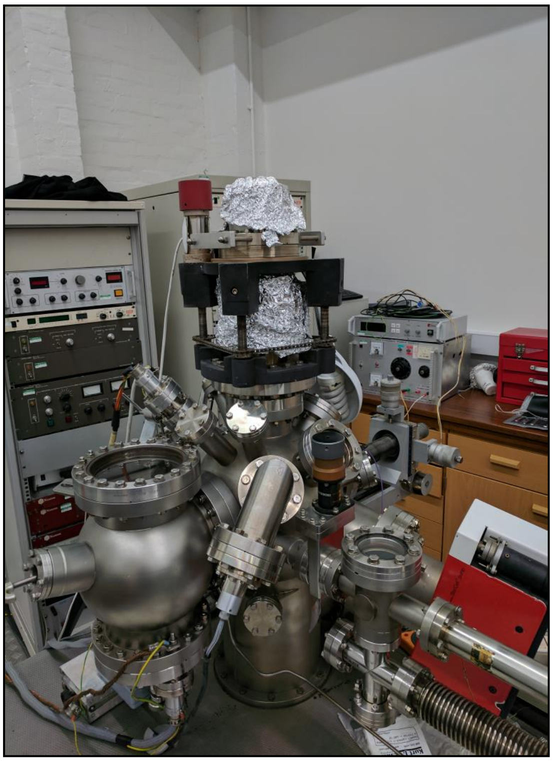

Figure 3 *Image of UHV chamber used in lab.*

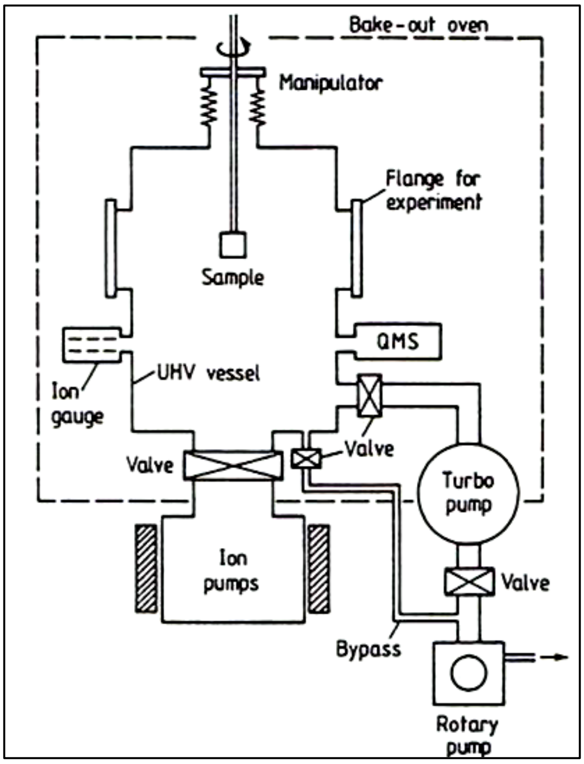

Figure 4 *Schematic view of an UHV system, including pumps QMS and pressure gauges* [2].

The UHV chamber is made of stainless steel, which does not corrode or rust as ordinary steel and has low rate of outgassing of absorbed gas. In addition to this the whole system is designed to be 'baked', this means the chamber can be heated to around 470K while vacuum pumps operate for around 24-36 hours [7]. This accelerates the desorption of water vapour and other gases from internal surfaces of the chamber, hence improving the resulting vacuum and allowing the system to reach ultrahigh vacuum conditions more rapidly. The chamber is baked when the chamber has been opened for modifications or repairs, and has hence been exposed to the external environment.

In addition to the pumps in the UHV chamber there are several other important instruments necessary for surface science experiments. The most notable of which are; the pressure gauges which monitor the ambient pressure inside the chamber, the Pirani gauge which measures pressures in the range 10^{-3}-100 mbar and the Ionization gauge which measures pressures in the range $10^{-4} – 10^{-10}$ mbar, a manipulator which is used for the mechanical movement of the sample within the chamber and finally a Quadrupole Mass Spectrometer (QMS) which is designed to monitor any contamination in the vacuum system. The QMS contains the basic components of four quadrupole rods which are pairwise biased with a superposition of a DC voltage and an AC component. For a given geometry of the QMS only ions of a particular mass-to-charge ratio can oscillate between the rods in stable orbits and reach the detector, whereas other ions oscillate in unstable orbits and hit the rods. A mass spectrum is obtained by monitoring the ions passing through the quadrupole as the DC and AC components on the rods are varied [2]. The QMS is used specifically for this project to check the cleanliness of the Ar^+.

2.2 Surface Preparation

The surface of the sample when exposed to the ambient gasses in the air becomes contaminated with oxides and carbides, therefore it needs to be thoroughly cleaned in both air prior to being inserted into the UHV chamber and cleaned further in UHV conditions before it can be accurately characterised. There are several steps to properly prepare a clean surface before it can be doped with the chosen dopant and analysed, the techniques used in this project are covered in this section.

First it is necessary to determine the crystallographic direction of the sample which is to be analysed. The specific orientation desired can be determined by Laue backscattering and the sample is cut along the required axis. In Laue backscattering a polychromatic x-ray beam impinges on a single crystal through a small hole in a disc-like detector, specific wavelengths within the spectrum of the beam reflect off the lattice planes of the crystal back onto the detector. From the resulting pattern the orientation of the crystal can be determined [8]. For example if there is a certain symmetry of the crystal that is of interest, the orientation at which that symmetry is observed would be the axis at which the sample is cut. For this project the Al_9CO_2 sample was cut in the (001) orientation. The orientation of a surface or a crystal plane may be defined by considering how the plane intersects the main crystallographic axes of the solid. The assignment of the Miller Indices, (hkl); a set of numbers which quantify the intercepts and hence may be used to uniquely identify the plane or surface. The cutting was done using a wire saw and the surface was then prepared by mechanical polishing with decreasing diamond grain sizes from 6 µm down to 0.25 µm followed by a final polishing step with Syton OP-S (Struers) [4]. When cutting the crystal in the (001) orientation we see a structure of alternating planes of pure Al and planes of Al mixed with Co, as shown in the produced Vesta model below (Fig 5,6).

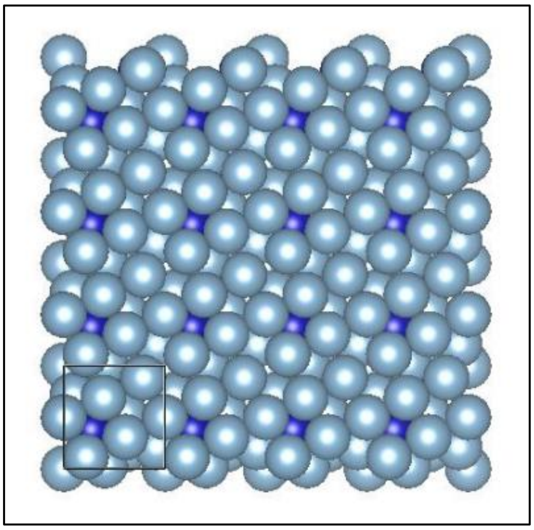

***Figure 5** VESTA model showing Al_9Co_2 (001) surface, light blue atoms corresponding to Al and darker blue corresponding to Co.*

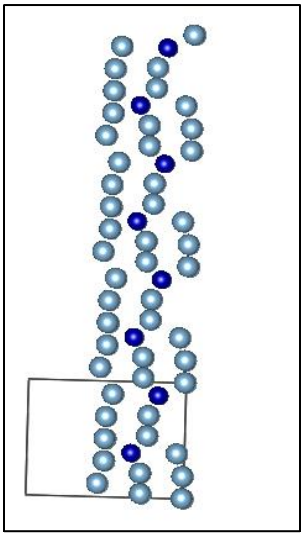

***Figure 6** side-on view of VESTA model of Al_9Co_2 (001) surface, illustrating how the structure of the surface arranges in planes of pure Al and planes of Al mixed with Co.*

The sample is then placed in the UHV chamber for further cleaning via sputtering and annealing cycles. First the surface is sputtered using an Ar^+ ions; sputtering is the bombardment of the top most layers of a surface with a noble gas which is ionised with an electron gun, this removes the top most layers of the surface and hence any contaminants embedded in the surface. Positive Argon ions are accelerated by a potential difference of a few kilovolts by placing a negative bias on sample surface [9]. The ion current and the duration of the bombardment depend on the kind of material and on the degree of contamination [2]. The surface is then annealed; annealing is when the surface is heated to facilitate diffusion of bulk atoms to remove defects and facilitate desorption of Ar^+ ions embedded on the surface from sputtering. Six cycles of Ar^+ ion sputtering were carried out for 30 min at an average Ar^+ pressure of $7.5x10^{-6}$ atm followed by annealing to different temperatures ranging from 943K to 953K, to obtain clean surface data. In between scans both Low Energy Electron Diffraction (LEED) and Scanning Tunnelling Microscopy (STM) data was taken to determine the local atomic arrangement and the surface composition to assess the overall cleanliness of the sample.

Thin films of elemental or molecular materials are deposited on a substrate by evaporation and condensation processes, Zinc phthalocyanine was heated to sublimation in the UHV chamber and the vapour condensed onto the substrate. The ZnPc was contained in a Tantalum foil packet which is attached to two wires, the wires have a current passed through them that provides enough heat for the ZnPc to sublime. The Al_9Co_2 crystal was kept at room temperature during the dosing. Initially the dosing was done for an arbitrary amount of time so that we could calculate the flux or the amount of molecules hitting the surface. Using STM, it is then possible to calculate how much of a monolayer has been dosed, for example 15 min gave a coverage of 0.8ML (monolayer). The preferred dosage of ZnPc was such that we achieved a coverage of between 0.3ML - 0.7ML which allows for measuring the molecular ordering and in addition to the substrate for analysis of adsorption sites.

2.3 Scanning Techniques

The Scanning Tunneling Microscope, developed by Binnig and Rohrer for which they were awarded the Nobel Prize in 1986, is a technique which allows direct imaging of a surface with atomic resolution [2]. The development of this technique was incredibly important in surface physics as before STM determining the atomic structure on the surface of a material was carried out by indirect imaging methods, and the use of calculations derived from models. STM imaging works on the principle of the quantum mechanical effect of tunnelling, this is when the wavelike properties of electron permit them to move beyond a potential barrier, where in classical mechanics it would not be possible. The microscope operates using an atomically sharp tip of approximately 10Å positioned within 1nm distance to the sample so that the electron wavefunctions of the tip and the sample overlap. With the application of a small bias on the tip electrons may tunnel across the potential gap from the sample to the tip, creating a 'tunnelling current'. The tunnelling current is proportional to the density of electrons at the surface of the sample [10]. There are two modes of operation for STM imaging; constant height mode and constant current mode. In constant height mode the tip scans in the xy-plane (x and y parallel to the surface) and the height above the surface (z normal to the surface) is kept fixed. The tunneling current is then plotted as a function of the position in the xy-plane. In constant current mode the distance between the tip and the surface is kept fixed so that the tunneling current is fixed. This is done using a feedback loop which monitors the tunneling current and in turn adjusts the tip-sample separation by moving the tip in the z-direction. The tunneling current is recorded and plotted a as function of the position in the xy-plane. For this experiment the STM was used in constant current mode.

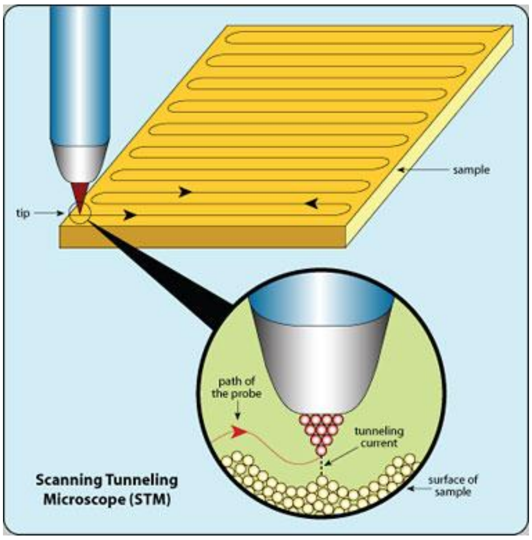

***Figure 7** Simple representation Scanning Tunnelling Microscopy and the path of the tip across the surface.*

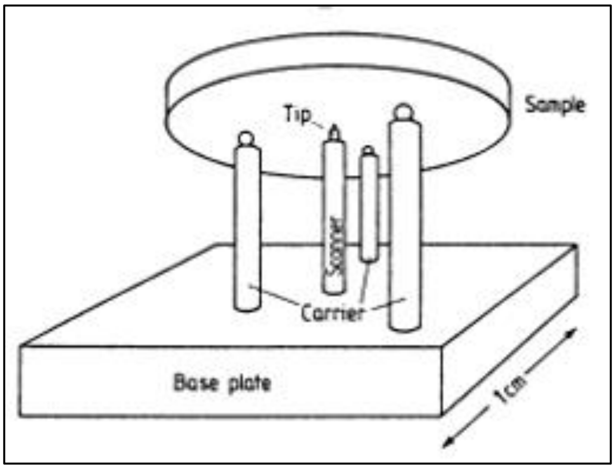

***Figure 8** Schematic of the three piezoelectric legs used for the microscopic movement of the sample, and the central scanning tip* [2].

To achieve atomic resolution images the movement of the tip across the surface must be highly sensitive, hence the movement of the tip must be controlled to within 1–2 Å. To achieve this the sample is mounted on a piezoelectrically driven support. Three metallic legs carrying a piezoelectric plate are used to achieve the movement of this support over distances of 100–1000 Å [2]. This is done via the piezoelectric effect. By compressing a piezoelectric crystal a potential difference is created between the sides of the crystal and conversely by placing a voltage across the crystal, it can compress or expand. These voltage-induced tensions are utilised for tip movement along the three axis (x,y and z) with an accuracy of better than 1 Å. This is achieved by varying the bias on the piezodrives by several tenths of a volt, from this we obtain a small angular tilt of the tip which over small distances is approximately horizontal motion. The tip material and how it is formed is also very important for obtaining atomic resolution images, for this experiment a Tungsten (W) tip which was chemically etched using potassium hydroxide (KOH) in water [11]. Chemical etching is a subtractive, tightly controlled corrosion process that can produce highly complex metal parts. The possible materials which can be used to make tips for STM imaging is limited due to the fact that atomic resolution images originate from p or 2d electron states on the tip, therefore only d-band metals can be used [12]. STM was used predominately during the experiment for both the clean and dosed images taken.

Low Energy Electron Diffraction (LEED) gives information about structure and morphology of surfaces. LEED operates via electrons which are emitted toward the sample from a hot filament and accelerated to a required energy. Electrons are incident on the sample are back scattered from the crystal surface in preferred directions according to Bragg diffraction conditions. Back scattered electrons are collected on a positively biased fluorescent screen, the positive bias accelerates the electrons sufficient kinetic energy to cause light emission. The pattern produced by these electrons can be used to determine the long range order of the surface and the surface unit cell [2]. Its purpose in the project was simply to quickly evaluate the cleanliness of the surface during the sputtering – annealing cleaning cycles in the UHV chamber, to see if further cycles were necessary.

2.4 Data Collection

The objective for this experiment, as stated previously, was to analyse adsorption sites on the substrate and to analyse the molecular diffusion of the ZnPc across the surface. For the first objective STM images of both the clean Al_9Co_2 surface and the dosed surface were taken. The clean surface data was analysed to determine what exactly we were observing, i.e. were we directly seeing the morphology of the Al_9Co_2 or whether they represent a cluster of atoms. This was then compared to the dosed surface images to investigate where on the surface the molecules adsorb and why.

To investigate the diffusivity of the surface several STM images of the same area were taken in succession and were made into ‘frames’ of a short video. The scan times were chosen to optimise the resolution of the images whilst taking into account the scan time could not be too long, as longer scanning times may mean missing some of the movement of the ZnPc molecules. This was repeated at three different temperatures; room temperature (RT), 312K and 350K. Using these videos it was possible to observe the molecules that were moving across the surface. To evaluate how the molecules diffuse and how they were affected by temperature the moving molecules were tracked frame by frame and the percentage of the total molecules that diffused were calculated for each video. In addition to this, using surface diffusion kinetics, the change of hopping rate with temperature was evaluated using proportionalities.

The software used for the analysis of all the images taken was WSxM. WSxM is computer software for scanning probe microscopy (SPM) and for nanotechnology [13]. For SPM experiments producing high-resolution images is the top priority so image processing is a central aspect of the software used for analysis, hence for this project WSxM was predominately used as image processing software. WSxM displays the STM images by assigning a different colour to a range of heights according to a colour palette, so the higher points on the images appear brighter. WSxM provides a number of processes to remove high frequency noise such as the ‘Gaussian Smooth’ function, this works by averaging image points with a Gaussian weight, and another method uses a two-dimensional fast Fourier transform that acts as a High-Pass filter, this means letting high frequencies pass by blocking low frequencies.

WSxM can also be used to measure distances on the image using the profile feature, by highlighting the area of interest by drawing a line across the image the software gives you the distance and the heights between the points via a graphical output. Other useful features for improving the crispness of the image were varying the contrast of the image and the plane function which removed any gradient in the image due to the direction in which the tip is scanning or if the image is taken early on and the piezo crystals aren't stabilised. All these features were utilised during image processing.

3 Results and Analysis

3.1 Clean Surface Data

The clean Al_9Co_2 STM data was taken before it was doped with the ZnPc and opened in the WSxM software. After processing the images using the WSxM features as stated previously, it was necessary to determine what was being observed. It was first thought that the bright regions were individual Al atoms and the dark regions were individual Co atoms. However, by analysing the image alongside the VESTA model and considering STM images show electronic density of states, not morphological features, it was concluded that what was being observed was clusters of atoms. Observing clusters of atoms rather than individual atoms is a feature seen frequently in STM images of quasicrystals and CMA's.

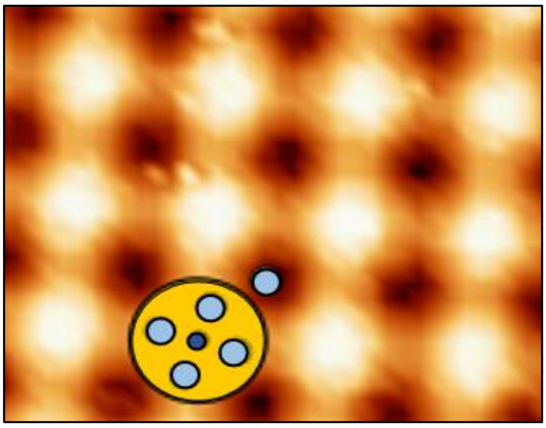

Figure 9 *STM scan of clean Al_9Co_2 (001) surface with schematic of the arrangement of atoms superimposed.*

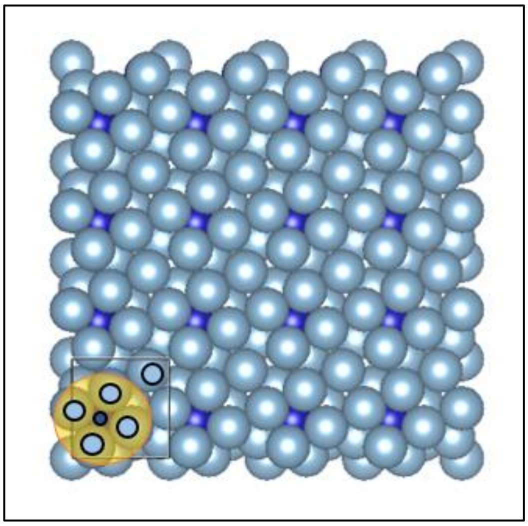

Figure 10 *VESTA model of Al_9Co_2 (001) surface with schematic of molecule arrangement superimposed.*

As can be seen in the figure above the bright regions of the clean image represent four Al atoms and a single subsurface Co atom, and the dark regions of the images is a lone Al atom.

There were also some terraces observed on the clean STM data, terraces can be considered planar defects in a bulk three-dimensional crystal. Separating terraces of different heights are steps which are line defects on a two-dimensional surface [14]. When moving from one terrace to another there is a mirror flip in the how the Al_9Co_2 are arranged, in other word a mirror symmetry is exhibited between the terraces. Examples of which are shown in the figures below.

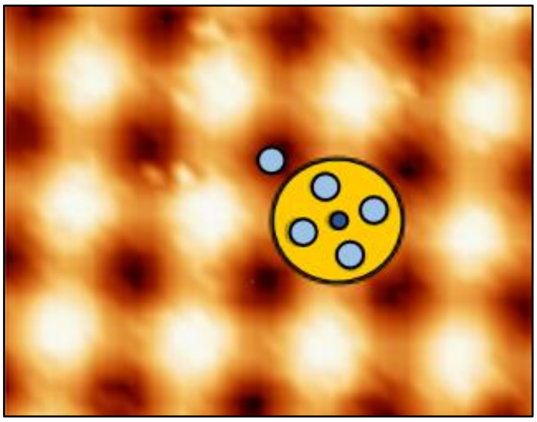

Figure 11 *STM scan of mirror flip of* Al_9Co_2 *(001) surface with schematic of the arrangement of atoms superimposed.*

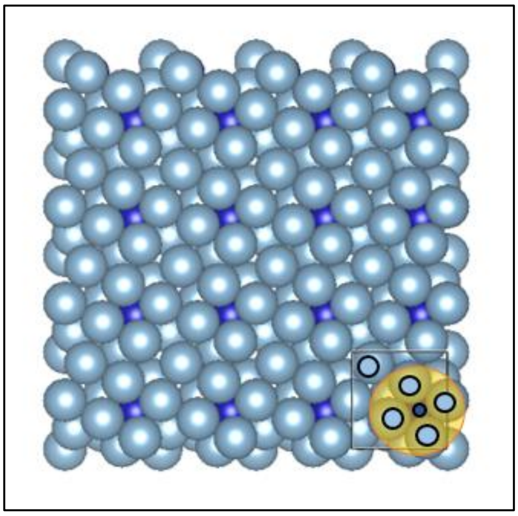

Figure 12 *mirrored VESTA model of* Al_9Co_2 *(001) surface with schematic of molecule arrangement*

The step heights were also measured using the profile feature of the WSxM software, five measurements were taken and averaged. The measured terrace height was 4.70 ± 0.04Å. The error on this value was calculated by the standard error on the mean. The measured terrace height was found to be consistent with literature value [4]. (Terrace measurement method shown in the Appendix)

Table 1 *shows measured heights of terrace*

Terrace Height (Å)	
4.67	
4.65	
4.70	
4.74	
4.73	
Average	4.70

3.2 Adsorption Sites

After the substrate has been dosed with ZnPc further STM data was taken and from this we observe that there are four different adsorption sites. The question is then if the molecules themselves have changed physically or are the differences due to the sites to which they have adsorbed. The differences are in fact due to the latter, the adsorption sites differ electronically. The four sites were; bright site, dark site, bright spin site and dark spin site (spin sites are where the ZnPc appear to be rotated by approximately 45°). The four different sites are show in the following figures shown below (Fig 13, 14, 15, 16).

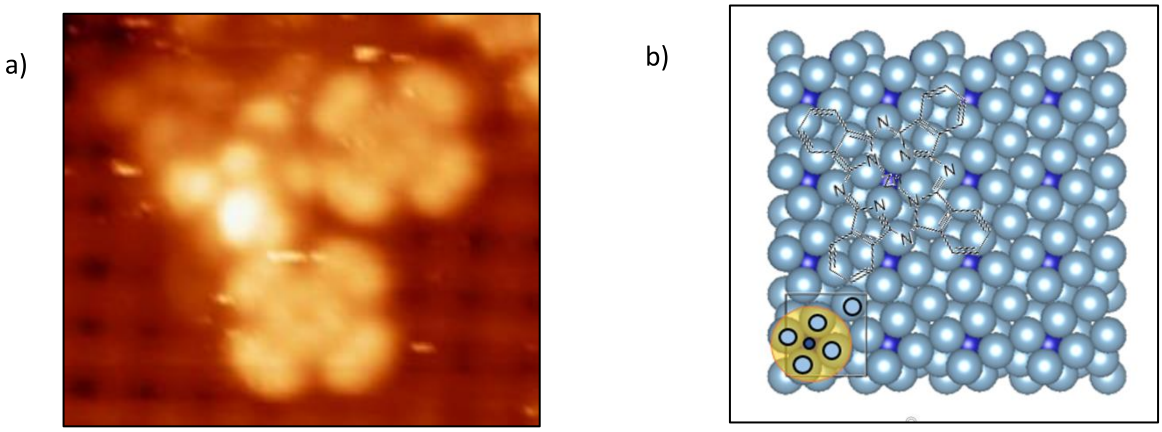

Figure 13 *a) STM image of bright adsorption site b) VESTA model of Al_9Co_2 surface with chemical structure of zinc phthalocyanine molecule superimposed illustrating the bright adsorption site.*

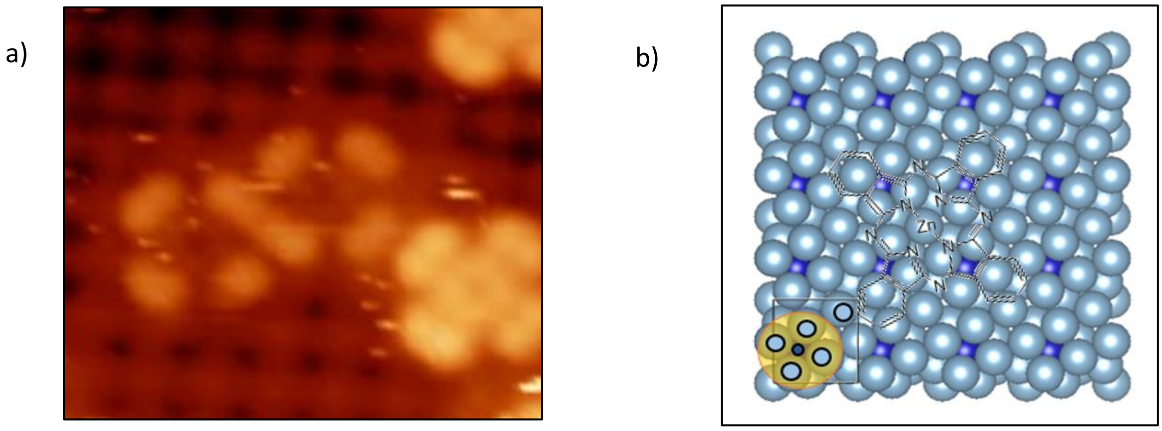

Figure 14 *a) STM image of dark adsorption site b) VESTA model of Al_9Co_2 surface with chemical structure of zinc phthalocyanine molecule superimposed illustrating the dark adsorption site.*

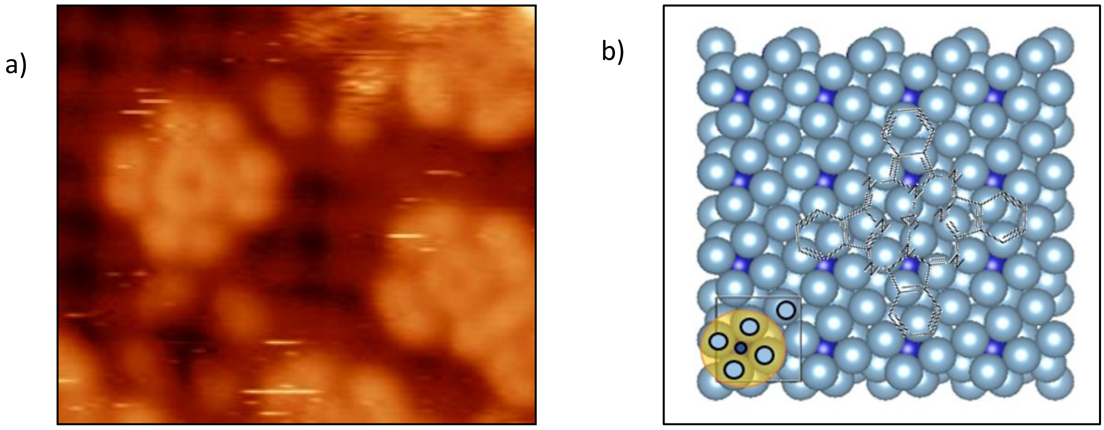

Figure 15 *a) STM image of bright spin adsorption site b) VESTA model of* Al_9Co_2 *surface with chemical structure of zinc phthalocyanine molecule superimposed illustrating the bright spin adsorption site.*

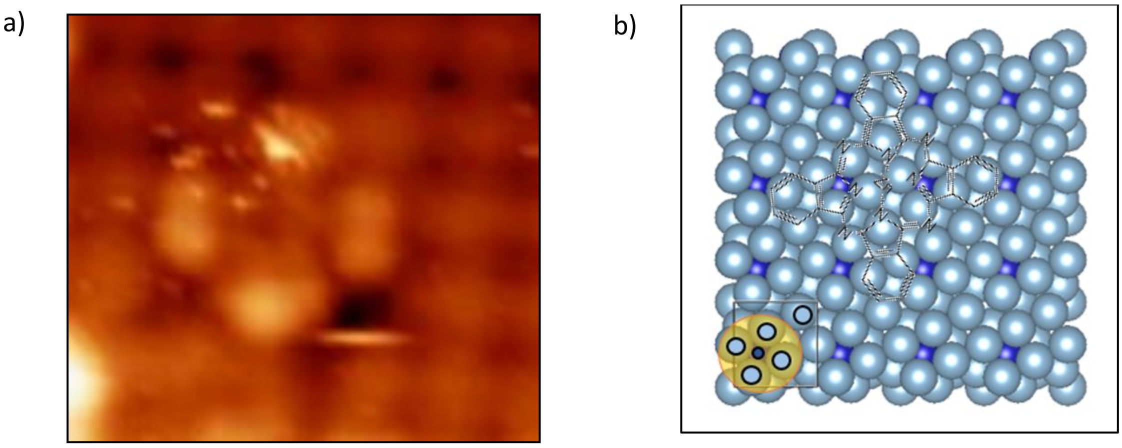

Figure 16 *a) STM image of dark spin adsorption site b) VESTA model of* Al_9Co_2 *surface with chemical structure of zinc phthalocyanine molecule superimposed illustrating the dark spin adsorption site.*

The bright sites occur because the central zinc atom in the ZnPc molecule is above a cluster of the four Al atoms and the subsurface Co atom. The dark sites occur because the central zinc atom is above a lone aluminium atom. Both the bright and dark spin sites occur because the central zinc atom is on a bridge site between two aluminium atoms. This can be seen in the STM data by highlighting a chain of bright regions of the clean surface showing they converge at the centre of a bright ZnPc adsorption site, the same can be shown for the dark sites.

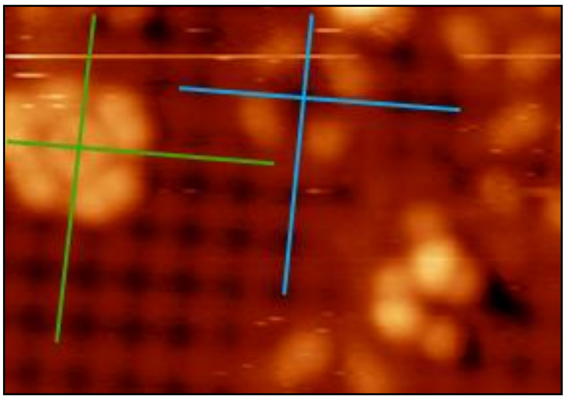

Figure 17 *Image showing how the bright and dark adsorption sites occur in STM.*

The statistics of how the molecular coverage is distributed between each adsorption site was also calculated showing that the most common adsorption site is the bright site (see Table 2).

***Table 2** shows the percentage of molecular coverage for each adsorption site.*

Adsorption Sites	Bright	Dark	Bright Spin	Dark Spin
% Molecular Coverage	70	20	7	3

In addition to these four adsorption sites it was also observed that a few of the ZnPc molecules exhibit a mirror flip. Only the molecules adsorbed to the bright and dark sites exhibit a mirror flip. This feature can be attributed to the mirror symmetry observed between the terraces of the surface, this suggests that the geometry of the surface plays a part in how the ZnPc molecule is adsorbed. The fact the spin sites do not exhibit a mirror flip could be due to geometrical or an additional electric effect.

3.3 Diffusion Data

The diffusion data was found by analysing the three videos at the different temperatures (RT, 312K and 350K) with the aim of relating how the molecules diffuse with increasing temperature. Initially the percentage of moving molecules was found by tracking the moving molecules from frame to frame. Spreadsheets were created to show how these molecules moved to the different adsorption sites, whether they jumped to an adjacent adsorption site (J), spun to the rotated adsorption site (S), or moved from bright to dark adsorption site (D) or vice versa (B). This allowed for the determination of the number of molecules moving in each video at each temperature. The total number of molecules in five frames of each video were counted and were averaged to give the average total number of molecules, from which a percentage was calculated. Raw data shown in the Appendix.

***Table 3** shows the percentage of diffusing molecules for varying temperature.*

Temperature (K)	RT	312	350
% Diffusing Molecules	15	38	88

As shown in Table 3 the percentage of diffusing molecules increases with increasing temperature. This is as expected from the laws of thermodynamics, as the temperature increases the energy of the ZnPc adatoms increases allowing them to separate from the bonds with the adsorption site more readily and hence diffuse across the surface more freely.

Surface diffusion kinetics is often described as adatoms which move from one adsorption site to adjacent adsorption sites via a jumping process [1]. The rate of these 'jumps' is characterised by the following equation;

$$\Gamma = \nu_0 e^{-\frac{E_{diff}}{k_B T}} \qquad (1)$$

Where Γ is the jump rate, ν_0 is the vibration frequency of the adatom, E_{diff} is the potential energy barrier, k_B is the Boltzmann constant and T is the temperature. This equation contains two factors which dictate the probability of the adatom making a successful jump, these are the attempt frequency and a thermodynamic factor [1]. The attempt frequency is simply the vibrational frequency of the adatom (ν_0) and the thermodynamic factor is the exponential so is dependent on E_{diff}, k_B and T. Both ν_0 and E_{diff} are unknown in this experiment meaning directly calculating the jump rate is not possible, however from Eq (1) it can be seen that the jump rate is proportional to temperature.

In place of a direct calculation, a ratio of the number of molecules moving (N_{mov}) to the number of stationary molecules (N_{stat}) was calculated. This was done by finding the sum of the molecules moving in each individual frame giving N_{mov}, subtracting this from the average total number of molecules in the frame to give N_{stat}, N_{mov}/N_{stat} was then calculated for each frame and averaged. This was repeated for each video so there was an average N_{mov}/N_{stat} given for each temperature.

Table 4 *shows N_{mov}/N_{stat} with varying temperature.*

Temperature (K)	RT	312	350
N_{mov}/N_{stat}	0.03	0.09	0.16

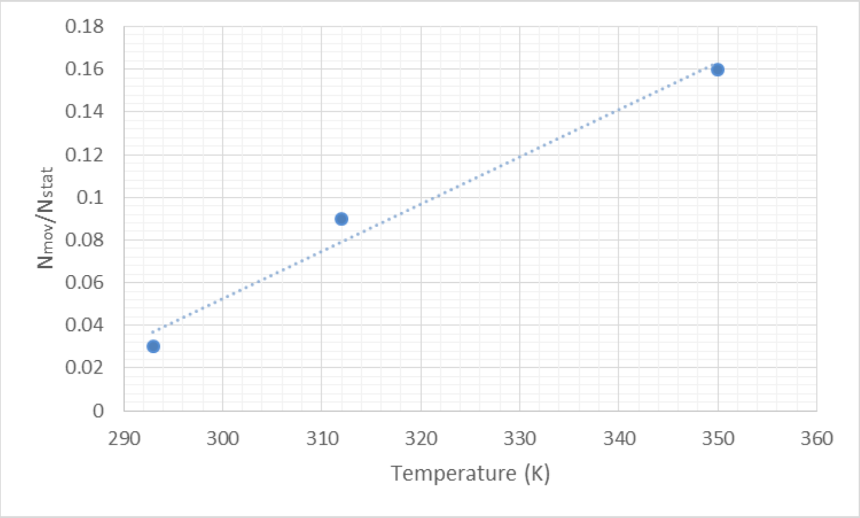

Figure 18 *Graph showing N_{mov}/N_{stat} with varying temperature.*

As can be seen from Table 4 the ratio of N_{mov}/N_{stat} increases with increasing temperature. What this ratio gives is an idea of how many molecules are moving per frame for the varying temperature, therefore this ratio is analogous to the jump rate. We know from Eq (1) that the jump rate increases with increasing temperature, we see a similar trend with the approximation hence the experimental data is consistent with surface diffusion theory. This ratio differs to the percentage calculated earlier as the percentage of diffusing molecules is represents the sum of diffusing molecules across all frames (i.e. the entire video) per temperature, however the ratio of N_{mov}/N_{stat} represents the number of molecules per individual frame.

Finally from analysing the diffusion data it was observed that there was a correlation between the diffusivity of the ZnPc molecules and the number of ZnPc molecules surrounding them. It appeared that some of the molecules which appeared in small close-packed clusters of ZnPc were less likely to diffuse than lone, separate ZnPc molecules. These clusters of ZnPc seemed to be bonded to each other preventing diffusion. This could possibly be the beginning of nucleation of the ZnPc on the substrate. Nucleation is the initial process that occurs in the formation of new self-organised structure, in which a small number of molecules become arranged in a characteristic pattern [15].

4 Discussion

Although using consecutive STM scans of the same surface is a useful method for analysing diffusivity of adatoms across the surface, the actual of the surface scanning does take a period of time. Therefore this means it is not possible to observe exactly how the molecules move across the surface, we only obtain a snapshot of their journey at that specific point. This does not affect the results obtained during this project as the values calculated were based on the number of molecules that diffuse not how they diffuse and the specifics of the diffusion mechanisms were not relevant to the project objectives.

Also, as often occurs in STM, there were some tip effects observed in the images. On few occasions the tip picked up the molecules meaning it was dragged across the surface of the sample, this issue was resolved by taking the position of the molecule at the end of its dragged path. In addition to this double-tip effect, this is when two atoms in the STM tip also experiences tunnelling meaning image appears to have a 'shadow', in other words the image is repeated in a slightly different position [10]. To combat this it was necessary to identify when this had occurred and to only take into account the real image not the 'shadow' image. This effect is one of the reasons why ensuring an atomically sharp tip is important.

Beyond this project there are plans to continue the research and experimentation on this Al_9Co_2 surface and ZnPc dopant combination. These future experiments include attempting to dose the substrate with a higher coverage of ZnPc, previous papers on zinc phthalocyanine has shown that there needs to be a critical coverage of the surface to initiate the growth of a monolayer [15]. The purpose of this would allow the observation of whether higher coverages would produce a well ordered film and to investigate if they arrange in a particular way which could have potential industrial applications. In addition to this, using the data analysing the change in diffusivity with temperature it can be found at what temperature the close-packed molecules start to diffuse. This would tell us about the bonding of the molecules to the surface, and the inter-molecular interaction. Finally using Density Functional Theory (DFT), DFT is a computational quantum mechanical modelling method which is used to investigate the electronic structure of systems [16]. These theoretical calculations would be able to calculate adsorption energies to determine favourable adsorption sites, calculate electron density, determine the nature of the bonding at each site, and simulate STM images. This is useful as it can be used to confirm experimental results displayed in this report and to explain some observations which weren't addressed here, for example confirming the adsorption sites and explain why the bright site was the most common adsorption site.

5 Conclusion

To summarize, in this report the basic principles of surface physics and it importance has been introduced, as well as providing an overview of the fundamental methods required to perform experiments on a surface. This includes; the necessity and the functionality of the different instruments used to obtain UHV conditions, the steps required to produce a clean surface, the different scanning techniques used, and image processing software and its features.

The objectives of this project were to analyse adsorption sites on the substrate and to analyse the molecular diffusion of the dopant across the surface of the substrate. To achieve these objectives; first, the clean, un-doped substrate was analysed, using STM images, in comparison with the doped substrate to investigate where the ZnPc adatom adsorbs on the surface, four adsorption sites were determined to be bright, dark, bright spin and dark spin sites. For the second objective the diffusivity of the molecules was investigated with change in temperature, using consecutive STM images forming videos take at three different temperatures; 293K, 312K and 350K. It was shown that the percentage of moving molecules increased with increasing temperature and the ratio of N_{mov}/N_{stat} was calculated which also increased with increasing temperature. This told us that both the number of diffusing molecules and the jump rate of the molecules increased with temperature.

The results of this project are part of a bigger investigation to determine how the surface is modulated by its complexity and whether it's possible for the ZnPc molecules to form a thin film which could be used industrially, hence finally the continuation of this project was discussed. Further experiments are planned to take place including dosing the substrate for higher coverages and to use theoretical calculations to better understand the surface, the adsorption mechanism, kinetics of diffusion and confirm the experimental data. Although this project requires further detailed study, these findings provide some insight into the understanding of the Al_9Co_2 (001) surface and the adsorption of zinc phthalocyanine and its behaviour.

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7 Appendix

1. Project Proposal

Zinc phthalocyanine on aluminium dosed complex metallic alloys.

Zinc phthalocyanine (ZnPc) is an organic semi-conductor which has been noted for its potential for photovoltaic applications. Organic semi-conductors are used in photovoltaic cells due to their flexibility in varying their electrical and optical properties; ZnPc is an attractive candidate for use in producing solar-cells as it is easily synthesised and is non-toxic and phthalocyanine is very durable.

Complex Metal Alloys (CMAs) are crystalline compounds characterised by having very large unit cells comprising of up to thousands of atoms therefore the periodicity of the crystals becomes irrelevant affecting the physical properties of the crystal. Quasicrystals are compounds whose structure is ordered but not periodic, this means Quasicrystals differ from CMAs in that they have no periodicity.

The aim of this experiment is to dose a quasiperiodic surface with ZnPc and investigate the ordering of the atoms and sites observed utilising Low Energy Electron Diffraction (LEED) and Scanning Tunnelling Microscopy (STM) data in ultra-high vacuum (UHV) conditions. The substrate used as the quasicrystal surface will be 2-fold AlPdMn with option of Al_9Co_2 CMA.

Timeline

Week 1	- Meet with supervisor - Carry out essential reading on surface structure Physics.
Week 2	- Discuss with supervisor specifics and overall objective of project. - Complete project proposal.
Week 3	- Clean surface. -Take STM and LEED images of clean surface.
Week 4	- Dose surface with monolayer of ZnPc. - Take STM images/ LEED pattern.
Week 5	- Repeat images of monolayer surface. - Begin analysis of images.
Week 6	-Change temperature of substrate while dosing. - Take STM images/LEED pattern.
Week 7	- Collect preliminary results. - Prepare oral presentation.
Week 8	- Oral Presentation.

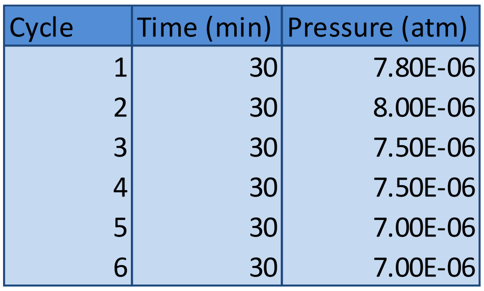
Week 9	- Continue analysis of images.
Week 10	- Begin collating results and research for report.
Week 11	- Continue work on report
Week 12	- Final hand in on 12/5/17

- Research and writing for report conducted continuously through semester.

2. Logbook Data

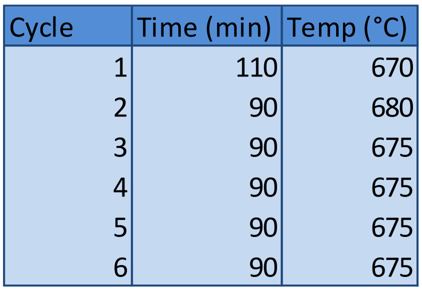
Raw data for cleaning in UHV

Table 5 *Time and pressure Ar^+ sputtering for each cycle.*



Cycle	Time (min)	Pressure (atm)
1	30	7.80E-06
2	30	8.00E-06
3	30	7.50E-06
4	30	7.50E-06
5	30	7.00E-06
6	30	7.00E-06

Table 6 *Time and temperature of annealing for each cycle.*



Cycle	Time (min)	Temp (°C)
1	110	670
2	90	680
3	90	675
4	90	675
5	90	675
6	90	675

3. STM scan times

***Table 7** RT scan times.*

Frame	Time (s)
ALL	45.22

***Table 8** 312K scan times.*

Frame	Time (s)
0-4	120.23
6--17	78.64

***Table 9** 350K scan times.*

Frame	Time (s)
0-6	26.21
7--30	13.11
31-37	26.21

4. Terrace Measurements

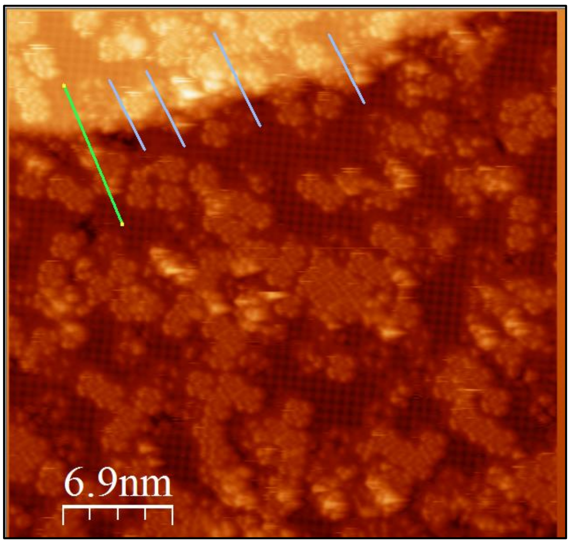
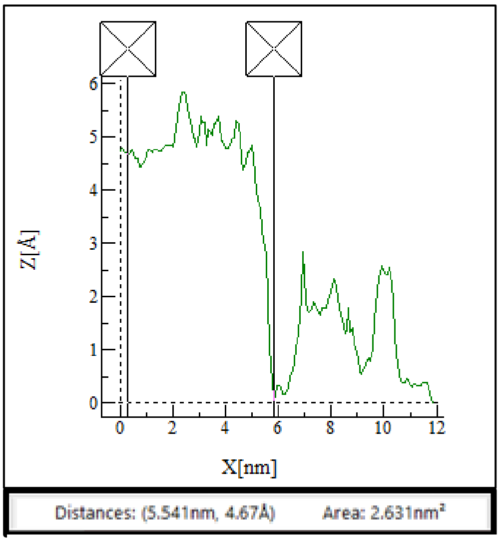


***Figure 16** shows the two terraces observed, and the line profiles used to measure the step height.*



Distances: (5.541nm, 4.67Å) Area: 2.631nm²

Figure 15 *shows an example of the graphical output of the profile and the measurements produced.*

Consistency check of experimental step height to literature value, showing that the two values are consistent.

$$|x_1 - x_2| < 3\sqrt{\Delta x_1^2 + \Delta x_2^2}$$

$$0 < 0.6$$

5. Raw diffusion data

Percentage of molecules moving data:

- Room Temperature

	Molecule #							
Frame #	1	2	3	4	5	6	7	8
0								
1						J		
2								
3	J							
4				J		S		
5							S	J
6	J							
7							S	
8					S	J	J	
9					J		S	
10					S		J	
11	S						J	
12	S	J					J	
13	J/D						S	
14		J					S	
15	J/B				J			
16	J		J					
17								J

Frame #	Total # Molecules	
1	51	
5	50	
9	52	
14	52	
17	52	
	Average	52

- 312K

	Molecule #																										
Frame #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
0																											
1	J	J			J	D	J	J								S	S							J	S		
2	J	J	S						S	S	J					S		J						J		J	
3	J	J	S		J		J	J	S	S		B				S		J						J			
4	J	J			J		J		S			J	S	J		S		J	J								J
5		J			J		J									S		J,D						S			
6		J					J	J																S			
7		J	J					J																S			D
8	J	J						J	S				S			S								J			
9	J	J					J	J								S								J			
10		J					J	J	S							S								S			
11		J			J				S							S								S			
12				J					S											J	S			J			
13				S			J									S								J			
14		S		S												S								J			
15		S					S		S							J								S			
16		J					J					J				J			J			S		S			
17		J														J			J	J		S		S			
18		S														J			J					S			
19		J					J							J		J			J					J			
20		S		J			S												S					J			
21		J		J			S					J				J			J					J			
22		J		J	S										D			B	S				J				
23		J			S		S	J							B								J	S			
24		J					J																	S			
25								J											J				J	J			
26																							J	S			
27		J					J	J																S			
28	J			J			S	J																			
29	J						S	J															J				
30		J																	J				J	J			

Frame #	Total # Molecule	
0	72	
10	70	
15	68	
20	72	
30	73	
	Average	71

- 350K

	Molecule #																							
Frame #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
0																								
1	J																J	J						
2	J										J													
3	J	J									J								J					
4	J	J								J	J								J	J				
5			J	J						J	J	J								J				
6					J						J	J							J	J				
7	J	J			J	J	J				J	J								J				
8	J	J			J	J	J					J							J	J	J			
9						J													J					
10					J	J						J							J					
11			J		J							J												
12			J	J		J	J	J												J				
13	J			J		J		J												J				
14						J		J																
15																					S			
16			J		J	J													J					
17				J	J									J										
18				J		J																		
19						J																		
20						J																		
21														J										
22						J															J			
23	J					J					J		J								J			
24											J		J								J			
25											J		J											
26											J										J			
27																					J			
28																						J		
29	J										J											J		
30													J	J								J		
31	J										J		J	J					J					
32														J		J								
33															J	J								
34	J								J						J	J								
35									J							J							J	J
36									J														J	J
37									J					J		S								

Frame #	Total # Molecule	
0	26	
5	27	
27	25	
30	26	
32	29	
	Average	27

Calculating N_{mov}/N_{stat} data:

- Room Temperature

Frame #	Nmov	Navg	Nstat	Nmov/Nstat
1	1	52	51	0.02
2	0	52	52	0.00
3	1	52	51	0.02
4	2	52	50	0.04
5	2	52	50	0.04
6	1	52	51	0.02
7	1	52	51	0.02
8	3	52	49	0.06
9	2	52	50	0.04
10	2	52	50	0.04
11	2	52	50	0.04
12	3	52	49	0.06
13	2	52	50	0.04
14	2	52	50	0.04
15	2	52	50	0.04
16	2	52	50	0.04
17	1	52	51	0.02

Avg Nmov/Nstat	
0.03	

- 312K

Frame #	Nmov	Navg	Nstat	Nmov/Nstat
1	9	71	62	0.15
2	10	71	61	0.16
3	11	71	60	0.18
4	12	71	59	0.20
5	6	71	65	0.09
6	4	71	67	0.06
7	4	71	67	0.06
8	7	71	64	0.11
9	6	71	65	0.09
10	6	71	65	0.09
11	5	71	66	0.08
12	5	71	66	0.08
13	4	71	67	0.06
14	4	71	67	0.06
15	5	71	66	0.08
16	7	71	64	0.11
17	6	71	65	0.09
18	4	71	67	0.06
19	6	71	65	0.09
20	5	71	66	0.08
21	7	71	64	0.11
22	5	71	66	0.08
23	6	71	65	0.09
24	3	71	68	0.04
25	4	71	67	0.06
26	2	71	69	0.03
27	4	71	67	0.06
28	4	71	67	0.06
29	4	71	67	0.06
30	4	71	67	0.06

Avg Nmov/Nstat	
0.9	

- 350K

Frame #	Nmov	Navg	Nstat	Nmov/Nstat
1	3	26	23	0.13
2	2	26	24	0.08
3	4	26	22	0.18
4	6	26	20	0.30
5	6	26	20	0.30
6	5	26	21	0.24
7	8	26	18	0.44
8	9	26	17	0.53
9	2	26	24	0.08
10	4	26	22	0.18
11	3	26	23	0.13
12	6	26	20	0.30
13	5	26	21	0.24
14	2	26	24	0.08
15	1	26	25	0.04
16	4	26	22	0.18
17	3	26	23	0.13
18	2	26	24	0.08
19	1	26	25	0.04
20	1	26	25	0.04
21	1	26	25	0.04
22	1	26	25	0.04
23	5	26	21	0.24
24	4	26	22	0.18
25	2	26	24	0.08
26	2	26	24	0.08
27	1	26	25	0.04
28	1	26	25	0.04
29	3	26	23	0.13
30	3	26	23	0.13
31	6	26	20	0.30
32	2	26	24	0.08
33	2	26	24	0.08
34	5	26	21	0.24
35	3	26	23	0.13
36	2	26	24	0.08
37	4	26	22	0.18

Avg Nmov/Nstat	
0.16	