Characterisation of Nanostructured Thin Films

Acknowledgements

1 Introduction

- Waffle about motivation for the project
    - Metal-Black films may have application for ... something.
        * Radiometer vanes, IR detectors
        * Number of applications where high absorbance into IR is required
        * These have all been studied before though.
    - The electron spectra of metal-blacks have not yet been examined.
    - Remarkable difference between Metal-Black films (bad vacuum) and normal metal films (UHV)
        * No (detailed/satisfactory) explanation (that I can find...) for difference
    - Talk about plasmonic based computing? Moore's law? Applications to thin film solar cells?

- Specific aims of project

    1. Surface density of states / band structure of Black-Au films using TCS (The main aim)
    2. Identification of plasmonic effects in Black-Au films (?) (If they even exist!)
        - Identify plasmonic effects in Au and Ag films with Ellipsometry (this is fairly simple to do)
    3. Combination of Ellipsometry and TCS to characterise thin films (not just Black-Au)
        - Ie: How can one technique be used to support the other?

- Structure of thesis

2 Overview of Theory

Summarise the literature, refer to past research etc

2.1 Electron Spectra of Solids and Surface

- Overview of section

In this section, we will first introduce the basic concepts needed to describe the electron spectra of solids. A short description of methods for calculating the electron spectra will be given, and the results shown by these calculations. We will then discuss the electron spectra for the near surface region of solids, compared to the "bulk" spectra far from the surface.

2.1.1 Description of Matter in the Solid State

- Define and describe solid geometrically
    - Basis + Lattice
    - Basis groups are assumed to be fixed relative to the lattice
- Describe general properties of the potentials seen by electrons in solids

In the simplest models, a solid is represented by an infinite crystalline lattice; a geometrically repeated arrangement of some basis group of atoms. The nuclei of atoms are assumed to remain in fixed positions.

The potential seen by an electron in the lattice is periodic. For a single nuclei, the potential seen by an electron is

2.1.2 Calculation of Electron Spectra

- Define electron spectra

    1.

- Free electron gas

- Free electron entering a periodic potential

- Potentials of real solids

- Single vs Multiple electrons

- Numerical calculations

    - TODO: Actually research this
    - Find a comparison with a real experimental result

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2.1.3 The Near-Surface Region

- Real solids have surfaces

- Differences between surface region and bulk

    - Resulting differences in potential

- How the electron spectra may differ from bulk values

    - Surface states
        * Tamm & Shockley States

In the preceeding sections, solids were assumed to have infinite spatial extent. In practice, any real solid occupies a finite volume in space. Any interactions between a solid and its environment take place at the surface of the solid. As the volume of the solid is decreased, the role of the surface region in determining the behaviour of the solid in its environment is increased.

- Description of the near surface region

    - All real solids occupy finite volumes in space.
    - The surface of a solid is important because interactions between the solid and its surroundings occur in the near surface region.
    - Characterised physically by:
        * Termination of periodic crystal lattice
        * Violation of geometric order
        * Distortion of interatomic distances and hence interaction forces
        * There is a transition "near surface" region between bulk and surface properties, roughly 5 atomic distances.
    - Potential seen by an electron at a surface can differ greatly from the bulk
    - $\implies$ the electron spectra of the near surface region differs from the bulk spectra
    - Simplest case: Step potential at surface.

- The Electron Spectra

    - Electron Spectra describes the energy eigenstates for an electron in a Bulk or Surface potential
    - Characterised by
        1. Energy dispersion $E(\boldsymbol{k})$
            * Dependence of Energy on electron wave vector
            * Obtained theoretically by solving Scrhrodinger's Equation
            * For a free electron gas, $E = \frac{\hbar^2 k^2}{2m}$
            * Periodic potential in bulk solid leads to band gap structure of $E(\boldsymbol{k})$
            * Periodic potential $\implies$ E is periodic. Only needs to be defined in first Brillouin zone.
        2. Density of States $N(E)$
            * $N(E) = \frac{\Delta N}{\Delta E} = \frac{1}{4\pi^3} \int_S \left(\frac{dE}{dk}\right)^{-1} dS$
            * Integral is in momentum space over the isoenergetic surface of energy E
            * For a free electron gas, $N(E) =$

- Surface states

- Simplest model: Step potential
- Two major models
  1. Tamm States: Periodic potential in solid, free space outside, jump at surface
     * Energy eigenvalues lie in the forbidden band of the bulk spectra
     * Attenuation of eigenvalues from surface to vacuum, oscillation of state within surface
     * Max electron density occurs on the crystal surface
  2. Shockley states: Potential of surface and bulk cells equal
     * Corresond to free valences (dangling bonds) at the surface
- Tamm and Shockley states arise from two extreme models (large change and small change respectively between bulk and surface). In reality, a combination of Tamm and Shockley states appear.
- These states arise from termination of the lattice; but the surface cells are assumed undistorted
- In reality surface cells are distorted by relaxation and reconstruction of the surface

- Main reference: Komolov "Total Current Spectroscopy"

- "Solid State Physics" textbooks and "Electron Spectroscopy" textbooks

2.2 Plasmonics

I really think I should actually find plasmonic effects before writing too much about them...

- Charge density oscillations

- Surface and bulk plasmons

- Pines and Bohm

- Review article from T.W.H Oates et al about using Ellipsometry to characterise plasmonic effects

2.3 Metallic-Black Thin Films

- How they are made (bad vacuum, in air or a noble gas)
  - If made in air, there are usually tungsten oxides present (from filament). Refer to paper by Pfund.
- Structural difference between Black-Au and "Shiny" (need a better term) Au
  - Can include electron microscopy images?
  - An actual photograph of a Black-Au film? Not necessary?
- Pfund (earliest publisher, preparation and general properties)
- Louis Harris (most research in 50s and 60s)
  - L. Harris mostly did transmission spectroscopy in the far infra red (well beyond the ellipsometer and Ocean Optics spectrometer ranges)
  - The really crappy measurements I did with the Ocean Optics spectrometer seem to agree with these measurements
    * L. Harris' λ has a range of 1nm to 100μm; my measurements are only to 1μm

* Agreement in first 1μm anyway
        * I should probably re-do those measurements with a less crappy setup, if I actually want to use them
    - Harris related the optical properties to the structure of the film (condensor strands) via the electronic properties

- Plasmonic effects - Deep R. Panjwani (honours thesis)

    - Not sure if I can use an honours thesis as a reference.
    - Concluded that surface plasmon resonance in Black-Au film on solar cells lead to increase in solar cell efficiency
    - Used simulation that modelled Black-Au film as spherical balls to show E field increased by plasmon resonance
        * Was this model appropriate? Black-Au is more "smoke" or "strand" like according to other references. Images also do not show "blob" like structure.
    - Need to read this reference more thoroughly

3 Experimental Techniques

3.1 Secondary Electron Spectroscopy

Secondary Electron Spectroscopy encompasses a large group of techniques used for studying the electron spectra of surfaces and solids. In these methods a beam of primary electrons is directed at the surface of a solid. The interactions between primary electrons and the surface give rise to a flux of secondary electrons scattered from the surface. Analysis of this secondary electron flux gives information about the interaction between primary electrons and the surface.

3.1.1 Electron-Surface Interactions

3.1.2 Methods of Secondary Electron Spectroscopy

Energy-resolved methods of Secondary Electron Spectroscopy are based upon observation of the secondary electron energy distribution at a fixed primary electron energy. The primary electron energy determines which processes are possible, whilst the observed distribution can be related to the probability distribution for the possible processes.

In contrast to Energy-resolved methods, Total Current (or Yield) methods are based on observation of the total current of secondary electrons as a function of primary electron energy. As the primary electron energy is increased, the threshold energies for particular processes are passed. This

Both Energy-resolved and Total Current methods can be performed

3.2 Total Current Secondary Electron Spectroscopy

Figure **??** shows a simplified schematic for the Total Current Spectroscopy experiments conducted during this study. Electrons are emitted from a cathode held at negative potential relative to the target. The electron beam is focused and accelerated onto the target by the electric field of an electron gun. A detector is used to measure the total current passing through the target.

3.2.1 Electron Optics

The electron gun used for this experiment was repurposed from an old Cathode-Ray Oscilloscope (CRO). Figure ?? shows a simplified diagram of the electron gun, whilst Figure ?? shows a photograph of the gun.

The full circuit diagram for the electron gun control circuit is shown in Appendix A.

3.2.2 Automatic Data Acquisition

In order to collect data on the large number of planned samples for the study, some form of automation was required. The automated system needed to be able to incrementally set the initial energy by controlling a power supply, and record the total current measured by an ammeter.

The available power supplies at CAMSP only featured analogue inputs for external control. This meant that a Digital to Analogue Convertor (DAC) card was needed to interface between the control computer and the power supply. In addition, the available instruments for current measurement at CAMSP produced analogue outputs. As a result, Analogue to Digital Convertors (ADCs) would be required to automate the recording of total current.

Although an external DAC/ADC box was already available for these purposes, initial tests showed that the ADCs on the box did not function. The decision was made to design and construct a custom DAC/ADC box, rather than wait up to two months for a commercial box to arrive. The design of the custom DAC/ADC box is discussed in detail in Appendix B, and the software written for the on-board microprocessor and the controlling computer are presented in Appendix C.

- Black-Au - 1e-2 mbar vacuum
- "Shiny" - 1e-6 / 1e-7
- Current of 3.5A through W wire filament spot welded onto Ta strips in turn spot welded to Mo posts
- Voltage through filament is 1 V; quote the power?
- Filament isotropically coats sample with desired material.
- Possibly get a curve of Au thickness estimated with Ellipsometry vs exposure time?
    - Probably too much work and too unreliable
    - Maybe do it, but only use 2/3 data points
    - Low priority

3.3 Electron Spectroscopy

Secondary electron spectroscopy methods are a broad class of methods which investigate surface electron spectra through observing processes in which the surface electrons participate directly [?].

Total Current Spectroscopy is a group of electron secondary

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- Total Current Spectroscopy methods measure the total current of secondary electrons as a function of primary electron energy.

- These methods are distinguished from "differential" methods (such as Auger electron spectroscopy and energy loss spectroscopy) which measure the secondary electron spectrum at a fixed primary electron energy.

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  – Low energy beam of electrons incident on sample
  – Measure slope of resulting I-V curve
  – Relate to density of states and electron band structure (Komolov chapter 3.2)

- Description of apparatus

  – Electron gun and filament
  – Electron gun control box
  – ADC/DAC control box and data processing

- Photographs vs Diagrams

  – Prefer diagrams to photographs
  – Especially for the ADC/DAC control box circuit. Because it looks like a horrible mess.

3.4   Ellipsometry and Transmission Spectroscopy

- Overview of techniques

- Description of apparatus (use VASE manual)

- Ocean Optics spectrometer? Usable?

- Application of Ellipsometry to finding plasmonic effects

  – Surface plasmons = E oscillation parallel to surface $\implies$ only p component of light excites plasmons

4   Experimental Results and Discussion

4.1   TCS Measurements

- TCS for Si

- TCS for Si + Au

- TCS for Si + Black-Au

- Affect of preparation pressure on TCS for Si + Black-Au

- Repeat for Si + Ag and Si + Black-Ag (?)

4.2 Ellipsometric Measurements

- Ellipsometry to estimate thickness of SiO2 layer on Si

- Estimate thickness of Au/Ag on Si+SiO2

- Ellipsometric measurements of Si+Black-Au/Ag

  – Modelling procedures to characterise Black-Au/Ag

- Ellipsometric measurements of Glass+Black-Au/Ag (?)

- Transmission spectra of Glass+Black-Au/Ag from earlier in year (?)

5 Achievements

- Deposition of thin films of Au and Black-Au in vacuum chamber

- Ellipsometric and spectroscopic measurements on these films

- Repurpose vacuum chamber for sample preparation and TCS experiments

- Designed and built electronics for TCS experiments

  – Electron gun control box
  – ADC/DAC box

- Wrote software for data aquisition and data processing

6 General notes

6.1 TCS

- Optimise setup of gun

  – Emission current. How much does it vary, why does it vary.
  – Why does Is/Ie curve shift with successive sweeps? Does sweep modify sample's surface?
  – Is sample holder acceptable? Are ceramic washers accumulating charge?
  – How do I tell when the setup is optimised... "The setup was optimised by looking for an S curve". Very scientific.
  – The gun was focused on the phosphor screen... and then I turned it around, changing the distance from the gun to the sample. Brilliant.

- Obtain TCS spectra for Si that compares well with literature

  – How to relate TCS spectrum to $n(E)$ and $E(\boldsymbol{k})$

- Prepare Au films, obtain TCS spectra that compares with literature

- Obtain TCS spectra of Black-Au films

- Use results to compare properties of films with results from other methods in the literature

- Uncertainties
  - Oscilloscope measurements of inputs to ADC channels under controlled conditions
    * Expected values are +/-3mV due to ADC channel, +/-300mV due to 610B, +/-1mV due to 602
    * 610B and 602 will probably be worse because they are ancient
    * There is about 200mV of noise between the GND of the ADC box and the electron control box.
    * How to reduce ground loops? Not much I can do. Rack is now also grounded to water pipe, but this doesn't seem to make a difference.
  - Stupid 50Hz AC noise... how to reduce with filters and/or averaging

- Create circuit diagrams for Electron gun circuit

- Create circuit diagrams for ADC/DAC box
  - Simulate behaviour of circuit
  - Use of instrumentation amplifier on ADC5 to make off-ground measurements
  - Use of low pass filter on ADC5

- Include references to all datasheets, etc

- Vacuum chamber
  - Base pressure with rotary pump? Was 1e-3 after 30 minutes at start of year, but probably introduced leaks since then
  - Lowest pressure achieved with turbo pump is 1.1e-7 mbar as of 25/07.
  - Viton gaskets on some seals. Copper on other.
  - Flanges:
    1. View window (large, view of sample & sputtering filaments)
    2. Rotation manipulator & sample mount
    3. Pump inlet
    4. Filament flanges 1 (used earlier in year, not anymore) and 2
    5. Inlet with leak valve (for introducing gases into chamber)
    6. Vent valve on turbo pump
    7. Electron gun flange
    8. View window (small, view of back of electron gun)

Appendix A - Electron Gun Control and Current Measurement Circuit

Figure **??** shows the complete electron gun control circuit. The circuit was designed and constructed as part of this project. The design is based upon examples found in [**?**] and [**?**].

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Appendix B - DAC/ADC Box - Hardware

Overview

In order to automate TCS experiments, both Digital to Analogue and Analogue to Digital Convertors were required (DAC and ADC). To provide these, a custom DAC/ADC Box was designed and constructed. The box can be controlled by any conventional computer with available RS-232 serial communication (COM) ports. Most modern computers no longer feature COM ports; a commercially available convertor can be used to interface between the box's RS-232 output and a standard Universal Serial Bus (USB) port.

The key components of the DAC/ADC box hardware include:

- Microprocessor (AVR Butterfly ATMega169)

- Four Analogue to Digital Converter (ADC) inputs

- Single Digital to Analogue Converter (DAC) output (Microchip MCP4922)

- Analogue electronics for amplification at ADC inputs and DAC outputs

- Seperate power supply circuitry for Digital and Analogue electronics

- RS-232 communications for control by a conventional PC or laptop

Microprocessor

The DAC/ADC box has been based upon Atmel's AVR Butterfly; an inexpensive and simple demonstration board for the ATMega169 16 Bit microprocessor. The features of the AVR Butterfly include easily accessible ports for Analogue to Digital Convertor (ADC) inputs and digital input/output, an onboard Universal Asynchronous Reciever/Transmitter (USART) for RS-232 serial communications, and a 6 character Liquid Crystal Display (LCD). The AVR Butterfly can be programmed using a conventional computer over the USART using a RS-232 COM port. For modern computers (which do not usually posess COM ports), a RS-232 to USB converter may be used.
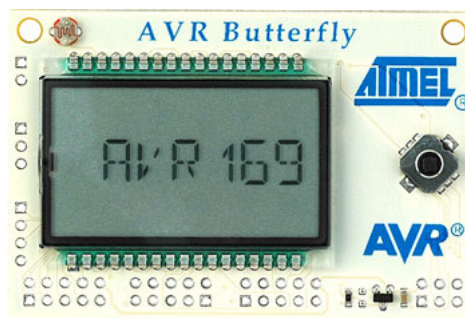
Unless otherwise stated, all voltage differences are specified relative to the power supply ground of the AVR Butterfly.

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ADC Inputs

The AVR Butterfly offers easy access to four of the ATMega169's ADCs through PORTF. Each ADC is capable of measuring voltages of $0 < V_{\text{adc}} < V_{cc}$ with 10 Bit resolution. For measuring voltages outside this range, some circuitry is required between the input voltage and the ADC input. In addition, it is desirable to provide the ADC with some form of input protection against accidental overloading. Figure 1 shows the input circuit which was used for three of the four available ADCs.
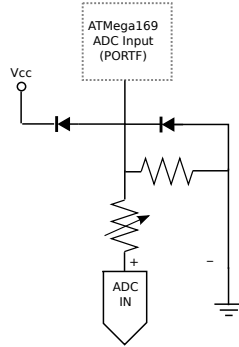

Figure 1: ADC4,6,7 Input

For making voltage measurements above V_{cc}, a voltage divider allows reduction of the voltage at the ADC. By constructing the voltage divider using a variable resistor, the range of measurable inputs could be manually adjusted.

The diodes shown in Figure Figure **??** ensure that the ADC is protected from accidental exposure to voltages outside the acceptable range. In normal operation both diodes are off. If V_{adc} were to become greater than the reference point V_{cc}, current would flow between the ADC input and the reference point, acting to reduce V_{adc} until it reached V_{cc}. Similarly, if V_{adc} fell below ground, current would flow from ground to the ADC input, acting to increase V_{adc} until it reached ground.

The voltage at the ADC input can be related to the input of the voltage divider using Kirchoff's Voltage Law and Ohm's Law:

$$V_{\text{adc}} = \frac{R_1}{R_1 + R_2} V_{\text{in}}$$

Where V_{in} is the voltage at the input of the circuit, R_1 is a fixed resistor, and R_2 is variable resistor.

V_{in} can be therefore be determined from the registered ADC counts by:

$$V_{\text{in}} = \frac{\text{ADC counts}}{2^{10}} \times \frac{R_1 + R_2}{R_1} V_{cc}$$

Differential ADC Input

During the testing of the TCS experimental apparatus, it became desirable to measure the emission current of the electron gun. The electrometer used for this current measurement was capable of producing an analogue output in the range of $0-1V$. However, the negative terminal of this output was not at ground potential, but rather at the same terminal as the negative input terminal. Directly connecting the electrometer output to one of the ADC inputs discussed above would create a short circuit between the initial energy power supply, and ground (refer to Figures **??** and **??**). Therefore, it was decided to add a differential stage before the input of one of the ADCs.

Figure **??** shows the modification made to the input for ADC5 on the AVR Butterfly. The original voltage divider and input protection discussed above are still present. The modifications include the addition of an instrumentation amplifier, and low pass filters.

The instrumentation amplifier consists of two stages of operational amplifiers (op-amps); input buffers, and a difference amplifier. The difference amplifier can be shown using the ideal op-amp model to produce an output voltage proportional to the difference between its inputs:

$$V_{out} = \frac{R_2}{R_1} (V_2 - V_1)$$

The two op-amps at the inputs to the differential amplifier act as unity gain buffers. Although the output of the unity gain buffer is equal to the input on its positive terminal, the buffer prevents current from flowing from the positive terminal to ground. With the buffer amplifiers absent, a current of: would flow between each of the input terminals and ground.

Instrumentation amplifiers are usually constructed in the schematic shown in Figure **??**. In this version, the gain of the amplifier can be changed by altering a single resistor. However, more resistors are required. The version actually constructed was designed based upon the small number of resistors available, within a short time frame. Although the design could have later been changed, this would have been of no real benefit, since there was no requirement to adjust the gain of the amplifier.

In principle, two ADC channels could be used to record the positive and negative outputs of the electrometer seperately, with differencing done in software. However this would require modification to the output cable of the electrometer, which may prove inconvenient for future uses.It was decided that the modification of the cable and added complexity of the software required would be more time consuming than differencing the two inputs using the hardware methods described above.

The low pass filters were added to the inputs of ADC5 after it was found that an unacceptable level of AC noise was being output by the electrometer. The level of noise was too high to be filtered in software, for reasons that will be discussed in Appendix D.

Power Supplies

Due to the presence of both analogue and digital electronics in the DAC/ADC box, three seperate supply voltages were required:

1. Digital logic in the range $3 \rightarrow 4.5$V

2. Positive op-amp supply in the range $10 \rightarrow 15$V

3. Negative op-amp supply in the range $-10 \rightarrow -15$V

Circuitry was designed which allowed two seperate single pole power supplies to be used for Digital logic and the op-amps. A dual 0-30V DC power supply has been used for both digital and analogue circuitry.

Logic Power Supply

The AVR Butterfly runs off $3V < V_{cc} < 4.5V$ DC. Since V_{cc} was also used as the reference voltage for the ADCs and DAC output, it was desirable that V_{cc} be kept constant, despite the absolute level of the power

supply. A $3.3V$ voltage regulator has been used for this purpose. The capacitor further smooths the output by shorting high frequency fluctuations to ground.

When the DAC/ADC box was first constructed V_{cc} was supplied by three $1.5V$ batteries. However, due to higher than expected power usage, and the unreliability of the voltage regulator as the input voltage fell below $4V$, inputs for an external power supply were later added.

Op-amp Power Supply

The DAC/ADC box circuitry involves several operational amplifiers (LF356), which require dual $\pm 10 - 15V$ supplies. As there were no dual $\pm$ power supplies available, a single $30V$ power supply was used, with the circuit shown in figure **??** used to produce $\pm 15V$ relative to ground.

The buffer amplifier ensures that negligable current can flow from the power supply into the logic and ADC circuits, whilst the capacitor removes high frequency fluctuations of the power supply relative to ground.

To simplify circuit diagrams, op-amps will be drawn with the power supply connections ommitted from this point onwards.

DAC Output

A commercial DAC board was used to produce the DAC output. The Microchip MCP4922 ET-Mini DAC is controlled by the AVR Butterfly using Motorola's Serial Peripheral Interface (SPI) Bus. The software used to implement SPI between the MCP4922 and the AVR Butterfly is discussed in Appendix D.

The ET-Mini DAC can only be powered off $3V$ to $5V$. Using $V_{cc} = 3.3V$ means that the DAC output cannot exceed $V_{cc} = 3.3V$. For TCS, energies of up to $15eV$ are required, so amplification of the DAC output was clearly necessary. A simple non-inverting amplifier with a manually adjustable gain was used to amplify the DAC output by a factor of three. This output was then used to control a laboratory power supply to produce the full range of initial energies.

RS-232 Communications

The AVR Butterfly features an onboard USART, which can be used both for programming and communication with the ATMega169 processor. The RS-232 communications requires only three wires; Recieve (RX), Transmit (TX) and a common ground.

The requirement that the AVR Butterfly share a common ground with the controlling computer lead to increased noise through ground loops. This is discussed in more detail in Appendix D.

Although the RS-232 is relatively simple to implement, which makes it ideal for non-proprietry microprocessor applications, most modern computers no longer feature RS-232 COM ports. Although a computer with COM ports was available at CAMSP, due to the extreme unreliability of this computer, it was quickly replaced with a laptop that did not possess COM ports, and a commercial RS-232 to USB converter was used to interface with the laptop.

References