B.Sc. (Hons) Physics Project

Thesis

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Characterisation of Nanostructured Thin Films

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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 a Surface

- 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 Preparation of samples

- 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

3.2 Total Current Spectroscopy

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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.

3.3 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

Appendix B - Data Aquisition Box (DAQ)

Overview

In order to automate recording of TCS data, a data aquisition box (DAQ) was designed and constructed. The DAQ consists of the following major components:

- Microprocessor (AVR Butterfly ATMega169)
- Four Analogue to Digital Converter (ADC) inputs
- Single Digital to Analogue Converter (DAC) output (Microchip MCP4922)
- RS-232 communications for control by a conventional PC or laptop
- Seperate Power supplies for digital and analogue electronics

Microprocessor

The DAQ has been built around an Atmel AVR Butterfly; an inexpensive and simple demonstration board for Atmel's 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.

Power Supplies

Two seperate power supplies are required for the DAQ, due to the presence of both digital and analogue electronics.

Logic Power Supply

The AVR Butterfly runs off $3V < V_{cc} < 5V$ DC. Since V_{cc} is also used as the reference voltage for the ADCs and DAC output, it is 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 DAQ 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 DAQ circuitry involves several operational amplifiers (LF356), which require dual $\pm 10 - 15V$ supplies. As there were no dual ± 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.

ADC Inputs

The AVR Butterfly offers easy access to four of the ATMega169's ADCs through PORTF. Each ADC is capable of measuring voltages (relative to ground) of $0 < V_{\text{adc}} < V_{cc}$ with 10 Bit resolution. A voltage divider constructed using a variable resistor allows manual adjustment of V_{adc} so that voltages greater than V_{cc} may still be measured. Diodes between the ADC input, and V_{cc} and ground, ensure that the ADC is protected from exposure to voltages outside the acceptable range. Figure **??** shows the typical input circuit, used for three of the four available ADCs. The voltage at the ADC is $V_{\text{adc}} = \frac{R_1}{R_1+R_2} V_{\text{in}}$, where V_{in} is the voltage at the input of the circuit.

For differential or "off-ground" voltage measurements, the fourth ADC input is passed through an instrumentation amplifier. Low pass filters on the input are used to reduce AC noise on the inputs. The buffer amplifiers ensure that negligable current flows through the measurement circuit to ground. Figure **??** shows the input circuit for off-ground voltage measurements. It is important to note that the circuit only functions when the input voltages are within the op-amp common-mode voltage range ($\pm 15V$).

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 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 Total Current Spectroscopy, 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 $3.3V$ DAC output to $10V$. This output was then used to control a GW-Instek GPS-1850D power supply.

References