B.Sc. (Hons) Physics Project

Thesis

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Characterisation of Nanostructured Thin Films

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1 Introduction

In this section I will give the overview of research done on metallic-black thin films, and explain the motivation for this project given the conclusions of past research.

- **Aim of Project**
  - The aim is to employ a range of techniques for characterisation of metallic thin films
  - In particular, metallic-black films vs "shiny" ("bright" might sound better)
  - TODO: Find a result (plasmonic behaviour?) so that I can say I was aiming to find it
- **Motivation for Project**
  - Talk about the surface playing an increasingly important role as semiconductor devices become smaller
  - Although metallic-black films are well known, they are extremely complicated and difficult to characterise

    * Fractal like structure, remarkable
    * Mechanism for formation is not well understood (Probably due to metallic nanoparticles having insufficient energy to form a regular lattice, due to energy losses through collisions with the high pressure atmosphere... I need to find a reference for this)
  - Metallic-black films have had numerous applications as good absorbers of optical wavelengths
    * High absorbsion coatings for radiometer vanes (Pfund)
    * Infra-red detectors; due to being almost transparent in the far infra-red
    * (Very recently; 2011), as scattering centres to increase the efficiency of thin film solar cells (Deep R Panjwani) *NOTE: This work was done in an honours thesis, although I believe the supervisor has also published a (much shorter) paper that I may reference if the honours thesis is not a good reference*
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- **Past Research**
  - Pfund - First mentions, preparation, optical transmission, resistivity
  - Harris - Later work, extends Pfund's experiments, introduces theoretical discussion of structure
  - Some other authors repeat or extend Harris' work. Metallic-black in different atmospheres, etc.
  - Modern research - Tends towards "artificially" blackened films, which suppress light reflection through plasmonic effects.
    * The goal is to develop films that exhibit similar effects to metallic-black films, but are simpler to describe theoretically. These films can then be used in applications requiring high absorbsion, as the original films
  - Can't find much research on plasmons in the "naturally" blackened films, except Panjwani *NOTE: Panjwani seems to have modelled the black films as semi-spherical nanoparticles, which in the light of other research (and the SEM images) may be inaccurate*

2 Overview of Theory

I will use this section to introduce general concepts of solid state physics. The Experimental Methods section will concentrate on the theory of each method, and how this relates to the overall theory.

- **What a nanostructured film is, how it differs from the bulk material**
  - The surface of a solid is the interface for physical/chemical interactions with it's surrounding environment
  - The physical and chemical properties of a material are largely determined by the electron spectra at the surface
    * Electron spectra is determined by the lattice potential
    * Characterised by
      1. Band structure of energy states - due to periodic lattice potential
      2. Density of States
    * Surface differs from bulk due to
      1. Termination of periodic lattice
      2. Adsorbed particles on surface (thin films)
      3. Relocation of lattice sites near the surface

* Band structure for Metal's vs Semi-conductors
  1. Metals:
  2. Semiconductors:

- **Surface Plasmons**
  - A collective oscillation of the electron gas in a metal
  - Surface plasmons are confined to the surface region; 2 dimensional, differs from bulk plasmons
  - Bohms and Ritchie
  - Past studies at CAMSP and UWA
  - May be caused due to excitations from
    1. Electrons - refer to next section
    2. Photons
       * Only light polarised in the plane of the surface can excite plasmons
       * Need to provide an extra wavevector to "match" the momenta of the photon and plasmon
       * Possibility for rough structure of metallic films to provide this wavevector
         · Refer to papers on "artificially" blackened films
         · Similar topic to Nikita's thesis; look at some of his references

- **Interactions between Electrons and Metallic Thin Films**
  1. Electron-Surface Interaction
     - How an incoming electron interacts with the surface as a whole
     - Elastic reflection from potential barrier
     - Phonon vibrations of lattice (quasi-elastic - low energy losses)
  2. Electron-Electron Interaction
     - Inelastic scattering processes determined by interaction of incoming electron with the electron gas
     - Low energy interactions (focus of low energy TCS)
       * Outer electron transitions between valence and conduction band
       *
     - Higher energy interactions (focus of other forms of 2nd Electron Spectroscopy)
       * Auger processes due to excitation of inner band electrons
       *
  3. General structure of secondary electron energy distribution (not investigated by TCS)
  4. Mention that secondary electrons have an angular distribution (not investigated by TCS)

3 Experimental Methods

Here I will give overviews of each method used in the study, including:

1. **Scanning Electron Microscopy**
   - Not used directly by me, so I will be very brief
   - Very useful for understanding the structural differences between metallic-black and metallic-bright films

2. **Total Current Spectroscopy**
   - Experimental setup
     - Refer to appendices for detailed description of control circuit and electron optics
   - Formation of the signal $S(E) = I(E)E$, and relation to theory of **Interactions between Electrons and Metallic Thin Films**
3. **Ellipsometry**
   - Optical technique commonly used for characterising thin films
     - Measures change in polarisation of light
       (a)
   - Sensitive to optical properties of materials; can be used to determine optical constants of a sample
     - Can relate the Ellipsometric parameters ψ and Δ to the optical constants (n or ϵ) of the
   - **Variable Angle Spectroscopic Ellipsometry**
     (a) Aquires a large amount of data automatically over different λ and θ
     (b) Using fitting algorithms, can construct multi-layered model of the surface, and determine characteristics of each layer based on known information
     (c) Can be complemented by reflection and transmission spectroscopy, performed with the same instrument
4. **Optical Spectroscopy**
   - Brief section, may not include if the other sections are sufficient
   - May combine with Ellipsometry section, since the Ellipsometer is used for these measurements
     - The important concepts will already have been discussed in the Ellipsometry section
     - Also used OceanOptics spectrometer early in the year, but repeated the same measurements using the Ellipsometer
     - Will need to review results before deciding whether to include or not

4 Results and Discussion

In this section I will discuss the results from each of the experimental methods described above, in order.

1. **SEM**
   - Images prepared by CMCA
     - The secondary electron current is imaged. The secondary electron current due to an Si substrate alone is substracted.
     - This gives an idea of the spatial distribution of the density of Au deposited on the Si substrate
     - TODO: Learn exactly how they are related... can I assume intensity $\propto$ density?
   - Discuss the clear difference in structure
     - Well defined regions (metallic nanoparticles) vs "smoke" like connected strands
   - Perform image fourier transforms
     - Au-Bright shows a elliptical distribution of low frequencies; indicates a preferred orientation for the Au

  - Au-Black shows a wider, circular distribution of low frequencies, and significantly larger high frequencies
  - Phase plots appear random except for some sharp lines near the centre of the FFT image (not sure how to interpret yet)
  - Validity of the transforms?
    * Error is introduced due to discontinuities in the periodic extension of the image
    * However, since the image is a region taken out of a periodically structured surface, these should be small
    * No window has been applied
  - Relation of image fourier transforms to theory?
    * I would love to be able to do this, but may not have time to understand how to do it
    * Can at least give a numerical approximation of fourier transform of density distribution of electron gas
    * Surely this can be used somehow? Approximate the structure factor of system?
    * Predict plasmonic behaviour?

2. **TCS**

- **TCS of Stainless Steel**
  - Establishes the location of the primary electron peak for Stainless steel
  - Useful because it allowed me to tell when the electron gun was focused so that the beam struck both the sample holder and the sample of interest
  - Appears to change over time; will discuss this behaviour below in relation to Si
- **TCS of Si substrate**
  - Changing of TCS vs Time
  - I am pretty sure it is not due to a "mistake" in the electron gun circuit
  - Possibly due to adsorbsion of oxide layer on the surface
  - I can show that depositing a thin layer of Au has the effect of "resetting" the TCS, which then begins to evolve over time.
  - I can also show that a sudden jump in E causes I to tend towards an assymptote
    * One reason why I changed to use E steps of 0.4V per second, instead of 2 V per
    * I probably won't discuss this in the thesis; maybe in an appendix
- **TCS of Au**

3. **Ellipsometry**

- **General Application to thin films**
  - **Jeremy's Sample - Permalloy**
    * Already have a good idea of the thicknesses
    * Can construct a model which gives good agreement with these thicknesses
    * Lorentz Oscillator model for the Permalloy
    * NOTE: I need to repeat this modelling procedure with more care
  - **Mikhail's Sample**
    * White Ni compared to Normal Ni
- **Metallic-Black Films**
  - Difficult to measure Au-black directly
  - Measured Au on Au-black on Si

- Compare with Au-bright on Si

4. **Optical Spectroscopy**
   - Need to review data before deciding whether to include this section
   - Mostly conducted transmission spectroscopy experiments
     - Transmission spectra of Au-Black agrees qualitatively with published spectra by Pfund and Harris
       - However, the range of my experiments is extremely small (visible wavelengths to short infra-red) compared to Harris (visible to extremely far infra-red)
     - Can show a difference between Au-Bright on Glass and Au-Black on Glass transmission spectra
     - Also have some transmission spectra of Ag, agree with expected Ag transmission spectra

5 Conclusion

In this section, I will hopefully find something intelligent to say about my results

Appendices

Mostly to do with the practical side of setting up the TCS experiment, and therefore (sadly) of little interest to the markers.

1. The TCS experiment in more detail
   (a) Electron Gun control circuit
   (b) Electron Optics - focusing the gun
      - This is extremely important for optimising the resolution of TCS
      - Include results of 2D simulation, but for qualitative purposes only (not actually used to focus the real gun)
   (c) ADC/DAC Card for control of E and measurement of $I(E)$ in TCS
2. Monitoring of the Vacuum Chamber pressure
   - This one will be short (I pointed a webcam at the pressure gauge, and wrote some software)
   - Include graphs of pressure over time
3. Theory
   - I may use this to put more detailed theory if the **Overview of Theory** section is too long
   - Then again, I may not have enough detailed theory to need this.
4. Software
   - I will probably just make all software available on my website and link to it
   - The software is not really written with "someone else may want to use this" in mind