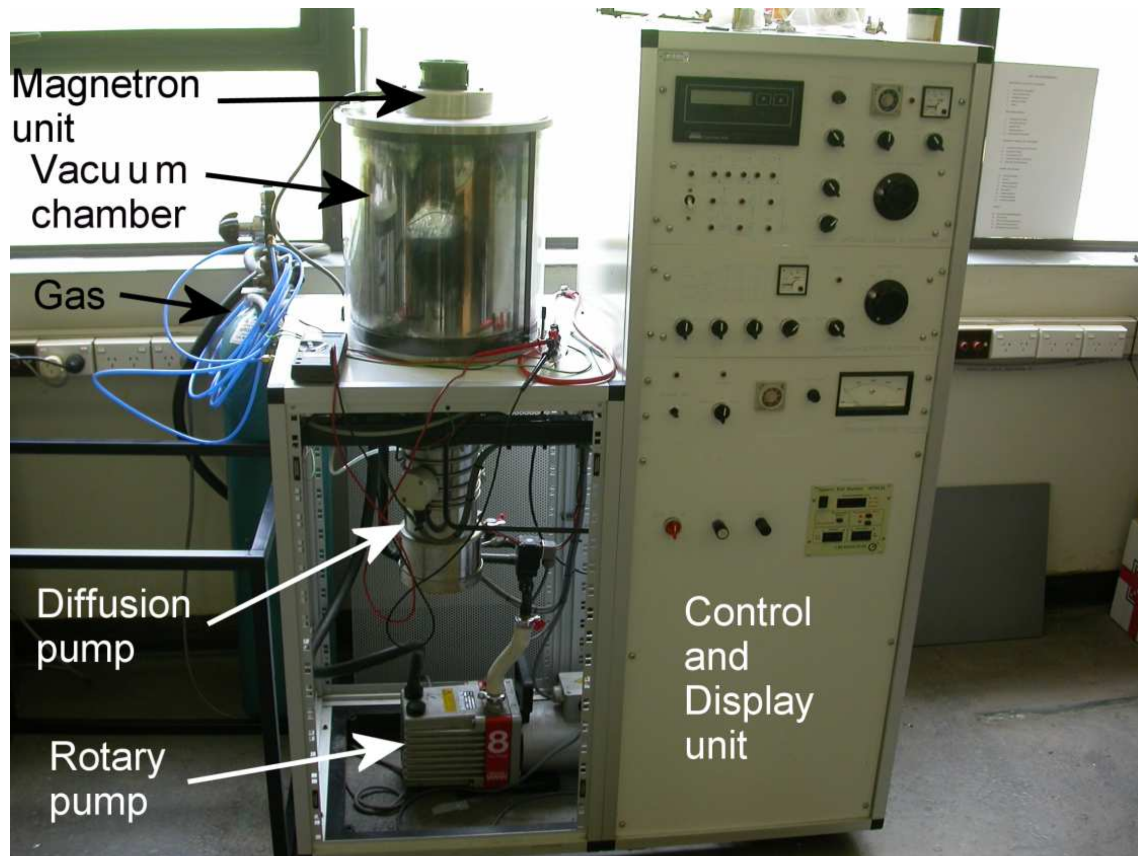
EXPERIMENT 30 — THIN FILM DEPOSITION



1 Equipment list

- Complete deposition system consisting of
  - Glass vacuum chamber
  - Protective clear plastic cylinder
  - Rotary and diffusion pumps and controllers
  - Evaporation unit and controller
  - Magnetron sputtering coating unit and controller
  - Crystal thickness monitor
- Aluminium wire for evaporation
- Tungsten wire for melting the aluminium
- Microscope slides on which to deposit aluminium and copper films
- Multimeter for measuring film resistance

Reference: H.-D. Liu, Y.-P. Zhao, G. Ramanath, S.P. Murarka, G.-C. Wang, *Thickness dependent electrical resistivity of ultrathin (<40 nm) Cu films*, Thin Solid Films 384, 151–156 (2001)

2 Aim

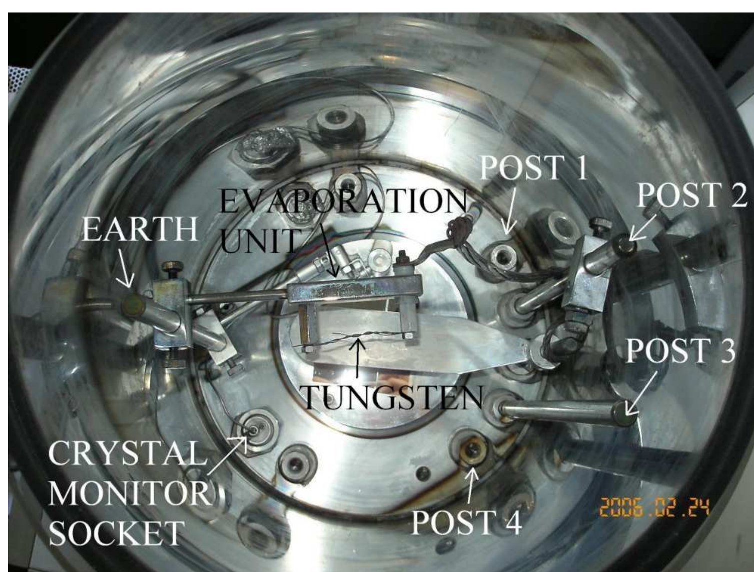
In this experiment you will use evaporative and magnetron sputtering techniques to produce thin films of copper and aluminium onto a glass slide (substrate is the technical word). Moreover, you will measure the resistance of the copper films during deposition in order to calculate the percolation threshold (more on this later). As a result, you will learn about the mechanism with which thin films are formed. From the resistance measurements you will then determine the bulk resistivity of copper and compare it to tabulated bulk values. Use your knowledge of the thin film deposition mechanism in order to explain any discrepancy between the two values.

3 Introduction

Thin film deposition technology is a major area of scientific research because of its wide range of applications such as optics, electronics (such as microprocessors), biotechnology and the tool manufacturing industry. Examples include anti-reflection coatings, interconnects for printed circuit boards, bio-compatible films for surgical implants and ultra-hard films decreasing the wear rate of machinery parts. The purpose of this experiment is to become familiar with vacuum equipment and processes, and two types of metal film deposition techniques - evaporation and sputtering.

Almost all film deposition techniques use vacuum conditions to reduce contamination and assist in film growth. In this experiment you will use a vacuum chamber to deposit aluminium contacts on a glass substrate by a process known as evaporative deposition. The contacts will then be used to monitor the conductivity of a copper film deposited using a magnetron sputter coater. The dynamics of thin film growth and the mechanisms of conductivity in discontinuous metal films will be investigated.

3.1 Evaporation System



Evaporation Unit

The apparatus consists of a glass cylinder vacuum chamber with a rotary vacuum pump, an oil vapour diffusion pump and pressure gauge. An evaporation source is mounted within the glass chamber. The source consists of twisted tungsten wires connected to a 60A current source at one end and the other end connected to earth. A small piece of aluminium wire

is wound around the tungsten, which becomes very hot when the current source is turned on. Since tungsten has a melting point of 3410 °C and aluminium has a boiling point of 2467 °C at atmospheric pressure the aluminium will boil before the tungsten begins to melt (in fact both these temperatures are reduced at low pressure). Aluminium vapour quickly fills the vacuum since there are no gas molecules with which to collide, finally condensing on any cold surface thus forming a metallic film.

3.2 Magnetron Sputter Coater

Mounted in the lid of the vacuum chamber is a magnetron sputter coater. This consists of a high voltage source for the production of an argon plasma by the initiation of a gas discharge between two electrodes. Positively charged argon ions are accelerated toward the negative electrode (cathode). The momentum transfer from argon ions with high kinetic energy impacting on the cathode can be enough to overcome the adhesion energy of the atoms in the solid. Atoms are dislodged (sputtered) from the surface and can be recondensed on another surface forming a thin film of the original solid.

Magnetic fields can significantly improve the efficiency of the ionization process in the discharge by confining the electron trajectories. A magnetic field perpendicular to the surface of the cathode will force electrons to spiral parallel to the cathode surface. This increases the chance of an ionizing collision with a gas atom near the cathode. For a given sputtering current, sputter rates are improved by an order of magnitude by the application of a magnetic field. Magnetically assisted sputtering units are termed “magnetrons”.

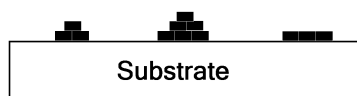
3.3 Crystal monitor

A vibrating-crystal film thickness monitor is mounted in the vacuum chamber. The vibration frequency of the crystal is proportional to the mass of material deposited on its surface. Calibrating this change in frequency to the atomic weight of the deposited material gives an accurate measure of the deposited film thickness. This method breaks down when the mass of the deposited material becomes too great and the calibration becomes non-linear. In this case the crystal needs to be replaced.

Crystal monitor

4 Theory

The early stages of film growth can be classified into two distinct types. Uniform coverage of the substrate by the depositing film followed by layer-by-layer growth, is called Frank-Van der Merwe growth mode. Film growth facilitated by nucleation and agglomeration of islands is called Volmer-Weber growth mode. A third mode (Stranski-Krastinov mode) describes a combination of the two. In general, metals on insulators grow via the Volmer-Weber growth mode.



Volmer-Weber growth

Nucleation of islands on the substrate surface occurs when a metal atom or ion imparts some or all of its kinetic energy to the substrate causing it to adsorb to the substrate surface. Adsorbed atoms (adatoms) are bound to the substrate by either Van der Waals or covalent forces. If the adatoms have enough residual kinetic energy to overcome these binding forces they can diffuse on the surface or desorb from the surface back into the gas phase. Diffusing atoms will move around the surface until they lose some energy or encounter a region where the binding forces are strong enough to pin them down. Surface defects such as grain boundary dislocations, step edges or surface impurities are common regions where diffusing adatoms will become bound. Bound adatoms themselves then become points where other diffusing adatoms can bind, thus nucleating islands.

Each nucleation site will become an island and each island will become a metal crystallite. The density of grain boundaries is determined by the size of the metal crystallites, which is initially determined by the distance between nucleation sites. Since bulk electrical resistance is dependant on scattering from grain boundaries and surfaces the nucleation process directly affects the electrical properties of the bulk material.

Island growth continues until the islands coalesce with one another, forming a contiguous film with connecting pathways. This point is often termed the percolation threshold. The film at this point is not continuous but contains holes that can become voids as film growth continues. Discontinuous films facilitate electronic conduction by electron tunnelling between islands. Tunneling probability is exponentially proportional to the distance between the islands, increasing to unity at the percolation threshold. At this point conduction is facilitated by classical processes in the conduction band of the solid. Resistance to conductivity in a contiguous film arises from electron scattering from grain boundaries, surfaces, voids and defects. When the film is thick enough that scattering from surfaces is negligible the resistivity will be equal to that of the bulk material of the film.

5 Procedure

5.1 Starting the vacuum system

The diffusion pump takes about 15 minutes to warm up so it is a good idea to do this early.

- Before you start, make sure that the water is turned on at the sink (water should be coming out of all hoses in the sink - only a trickle is needed). This provides cooling for the diffusion pump.
- Switch on the main power switch on the coater unit
- Switch on the rotary pump ("pumps" switch to "rotary on")

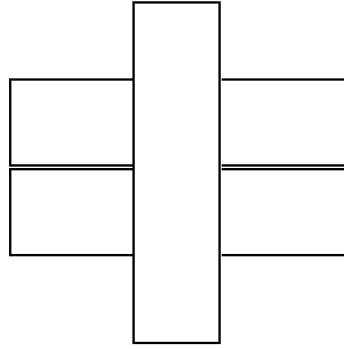
- Open the backing valve to the diffusion pump ("diff pump backing valve" switch to "open")
- Switch on the diffusion pump ("pumps" switch to "diff pump")

There should now be four red lights showing on the circuit diagram on the top panel of the unit (rotary pump, pump valve, backing valve and diffusion pump) and also the "power on" light at top left. If any other lights are observed ask a demonstrator to check the system. After 15 minutes the diffusion pump should be warmed up. The vacuum system will then be on stand-by for pumping the chamber. In the interim the glass substrates can be prepared.

5.2 Substrate preparation

Thin film growth and adhesion is fundamentally related to the substrate surface conditions. It is therefore crucial to thoroughly clean the substrate before the deposition process. In industry this is often done by plasma etching impurities from the surface. We will be a little less thorough here, using alcohol and a tissue.

- Clean two glass microscope slides thoroughly with ethanol and a "kimwipe" and allow to dry.
- Now remove the stainless-steel lid of the vacuum chamber. This can be difficult and it is important not to damage the glass cylinder. ASK A DEMONSTRATOR IF YOU HAVE TROUBLE. This is done by holding the sides of the lid and pulling vertically upward. When the lid is at least 5cms clear of the top of the glass cylinder, rotate the lid around to the left and allow it to slide back down the support post.
- The alligator clips and crystal monitor may still be inside the chamber from a previous experiment. Reach inside the cylinder and remove them both by loosening the blocks from the posts. The crystal monitor is unplugged by gently pulling the plug out of its socket at the base of the chamber. Place these parts aside until later.
- Using some paper towel, clean the inside of the glass vacuum chamber on the side closest to you and the rear side nearest the window, so you can see what is going on inside the chamber.
- Aluminium oxidises quickly and is chemically un-reactive, but it is still good practice to avoid inhalation of metal dust.
- Undo the evaporation holder earth lead.
- Loosen the evaporation holder at the support post and slide it up and remove it from the chamber.
- Twist a 3 cm piece of aluminium wire around the tungsten wire. If the tungsten wire is broken it will need to be replaced. Take care not to damage the ceramic insulator if replacing the tungsten.
- Place the two clean glass slides side by side in the centre of the circular substrate holder, avoiding touching the slide surfaces.
- Place a third slide across the middle of the two clean slides. This will act as a shadow mask for the other slides and leave a 2.5 cm square of uncoated glass with aluminium contacts at either end.



Crossed glass slide arrangement

- Return the evaporation unit to the chamber. You want to connect the evaporation unit between the earth post and either post 2 or 3. If any of the posts is in the wrong place then simply unscrew it and move it.
- Now tighten the tungsten evaporation unit in place about 10 cm above the glass slides.
- Cover the crystal monitor plugs with a small piece of aluminium foil to avoid a short circuit occurring when aluminium deposition starts.
- Replace the lid of the vacuum chamber.

5.3 Chamber evacuation

The chamber is now ready to be evacuated. The pumps should by now be warm enough to operate.

- Close the diffusion pump backing valve. This should not be left closed for more than about ten minutes.
- Check that the black air inlet valve at the bottom of the panel is shut and that the gas inlet switch beside it is off.
- Open the chamber roughing valve and observe the pressure. The pressure should begin to reduce after about 30 seconds. If not, check the lid is properly down, or ask a demonstrator to help.
- When the gauge shows a pressure of 1×10^{-1} mbar or less, close the roughing valve.
- Open the backing valve, returning the vacuum system to stand-by.
- Open the Chamber Isolation Valve. It is important that the pressure is below 1×10^{-1} mbar when the valve is opened.
- When the pressure in the chamber drops to below 1×10^{-4} mbar the system is ready to begin the evaporation process. You will need to change the detector on the pressure gauge to see the pressure below 1×10^{-3} mbar.

5.4 Evaporative deposition of aluminium electrodes

Evaporation is achieved by resistively heating the tungsten electrode. If the current through the tungsten is too high the tungsten will break and you will have to start again after replacing it.

- Check that the “Source A Control” knob is set to zero.
- Switch “Source A Select” to “Cont. on”. The source A light should illuminate. If not then you probably connected to the ”Source B” post. In this case go to the “Source B Control” knob.
- Turn the control knob to 30 and observe the tungsten filament glowing red after a few seconds. If this process is not observed or slow, the current can be increased slightly however the control knob should not be turned above 50. If the filament has been used many times it will become brittle and may break in which case it will need to be replaced.
- After a few seconds of the tungsten glowing you should observe the aluminium wire begin to melt and evaporate. When the inside of the glass tube turns silver/black so that the evaporation unit is no longer visible the current control knob should be returned to zero.
- Switch off the source (“Source A select” to “off”).
- Close the chamber isolation valve, which returns the vacuum system to stand-by (four red lights).

The chamber is now ready to be vented. It is important that the chamber is isolated from the pumping system before air is admitted or **the diffusion pump may be damaged**. Double check that the chamber isolation valve light is NOT on. The air inlet valve is located on the bottom panel of the instrument. Slowly open the valve to admit air into the chamber. The evaporation unit will be VERY HOT for a number of minutes after the deposition process. Wait at least 10 minutes before you open the chamber lid, then remove the evaporation unit, the glass tube and the glass slides.

You should now have two glass slides with aluminium contacts and an uncoated 25mm square in the middle of each contact. The next stage will be to deposit a thin metal film from a magnetron sputter coater whilst monitoring the conductivity of the film.

5.5 Film deposition by magnetron sputtering and in-situ conductivity measurement

Question: Explain why different materials exhibit different sputtering rates.

The calibration factor should be pre-set for copper deposition. The crystal should be the same distance from the source as the substrate. An error in the measurement arises at low film coverage due to a difference in the probability of atoms sticking to different substrates (otherwise known as the “sticking co-efficient”).

You will now monitor the conductivity of a magnetron deposited ultra-thin copper film in-situ. The evaporation unit should already be removed from the chamber and the vacuum system should be on stand-by (remember to warm up the pumps if you are performing this section on a different day to the evaporation section).

- Plug the crystal monitor into the plug on the rear of the base inside the vacuum chamber and attach the support arm to the Earth post. The crystal should be at least 10 cm from the top of the chamber and facing upright.
- Switch on the crystal monitor control unit (Xtal) at the bottom of the coater unit.
- Re-zero the film thickness.

- Replace the alligator clips back into the chamber on the posts that connect to posts 1 and 4, which connect to the red and black wires that will be connected to the mulitmeter.
- Taking care not to touch the uncoated area of the slide, attach the two aluminised contact pads of one of the glass slides to the two alligator clips. Make sure that the coated side of the slide is facing upward.
- The magnetron source is located slightly to the rear of the chamber lid. Position the crystal monitor and the slide, side-by-side, at least 10 cm from the top of the chamber and toward the rear of the vessel. If the crystal monitor is too close to the magnetron source it will act as an electrode and initiate a glow discharge, which could damage the crystal.
- Replace the lid of the chamber and check that the substrate and crystal monitor are below the centre of the magnetron source and also equal distance away. The lid can be rotated somewhat to achieve the optimal positioning.
- Pump down the chamber as in section 5.3
- When the pressure is below 1×10^{-4} mbar, argon can be introduced into the chamber by switching the gas inlet switch on the bottom panel of the deposition unit. Make sure the argon flow control knob is turned down before opening the gas inlet switch. Do not turn the argon flow know off too hard or you may damage the needle in the valve.
- Adjust the argon flow until the pressure in the chamber is around 5×10^{-2} mbar.
- Switch on the sputtering unit power and check that the current knob is fully counter-clockwise.
- Turn the "sputtering" switch to "continuous" and slowly increase the sputter current to 100mA. You should observe a purple glow discharge initiated at the cathode surface. Note the toroidal shape of the plasma that is concentrated in the region of high magnetic field. If a plasma is not observed check that the "auto pump-down" switch is set to "on". If there is still no plasma observed ask a demonstrator to help.
- Plug in the black and red lead to the multimeter inputs.
- Observing the film thickness on the crystal monitor, turn the magnetron current to zero when the film thickness reaches 1 nm. The plasma will interfere with the multimeter resistance reading so the measurements must be made with the plasma turned off.
- Take data of film resistance versus thickness for intervals of 0.2 nm to a resistance of about 1 kΩ.
- Comment on any observations of changes in resistance with time as you take your measurements.
- Continue to take data in 0.5 nm intervals until the film thickness reaches 10 nm.
- Plot your results.
- Estimate errors in your resistance values in terms of the short circuit resistance you measured earlier.

- Make a plot of film resistance vs thickness.
- Estimate the film thickness from the steepest part of the curve, which is the percolation threshold.
- By considering the film growth processes described in the Theory section and the way in which the crystal monitor measures thickness, can you think of any uncertainties that may be present in your estimate?
- What properties of the surface and the film will affect the percolation threshold?
- Multiply the resistance by the film thickness to obtain values of the film resistivity, ρ in Ωm.
- Plot ρ vs film thickness and estimate the bulk film resistivity for copper by determining where the plot will flatten out. Compare it with the published value in Handbook of Physical constants. Explain any discrepancy.
- Explain why the resistivity reduces with film thickness to a minimum value.

5.6 Shutdown

- With the vacuum system in stand-by mode, switch off the diffusion pump.
- Leave the backing valve open and the backing pump running for ten minutes while the diffusion pump cools down, then switch off both of them. One of the demonstrators will turn off the cooling water at the end of the lab.