2 Materials under study and their development

The materials which are selected for the present study are: (i) Copper nitride (Cu$_3$N) (ii) Copper Oxides (Cu$_2$O and CuO) (iv) Silicon dioxide (SiO$_2$), (iii) Hydrogenated amorphous carbon (a-C:H), (iv) Amorphous carbon (a-C), (v) Diamond, (vi) Graphite and (vii) Fullerene (C$_{60}$). Apart from graphite, all the materials are in thin film form and have been deposited by different thin film deposition techniques. Among these films, Cu$_3$N, Cu$_2$O, CuO, a-C and C$_{60}$ are prepared at NSC. Rest of the films are made at other laboratories. Films of a-C:H are made in Gintic Institute of Technology, Singapore and the diamond films have been prepared at Indian Institute of Technology (IIT), Bombay.

The deposition of the films with a brief description of the respective techniques are discussed in this chapter in four sections: (i) RF reactive sputtering technique and preparation of Cu$_3$N, Cu$_2$O and CuO films, (ii) vacuum evaporation technique and deposition of SiO$_2$, a-C and C$_{60}$ films, (iii) magnetron sputtering technique and deposition of a-C:H films and (iv) Hot filament chemical vapor deposition (HFCVD) technique and deposition of diamond films.
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2.1 RF Reactive sputtering technique and development of Cu$_3$N, Cu$_2$O and CuO thin films.

In this section, first the rf sputtering technique will be discussed followed by the description of sputtering unit and the deposition process of Cu$_3$N, Cu$_2$O and CuO films.

2.1.1 RF sputtering technique

The rf sputtering method was initially developed for depositing insulating films. In a conventional dc sputtering system, if an insulator is used as a sputtering target, a positive surface charge is built up on the front surface of the insulator during ion bombardment, hindering the sputtering process. RF sputtering system gets rid of this difficulty. The rf potential is applied to an electrode. At rf potentials, the electrons oscillating in the alternating field have sufficient energies to cause ionizing collisions and the discharge will be self sustained. RF sputtering essentially works because the target self biases to a negative potential. Negative target bias is a consequence of the fact that electrons are considerably more mobile than ions. As the rf signal is applied to the target, a large initial electron current is drawn during the positive half of the cycle. However, only a small ion current flows during the second half of the cycle. This would result in a net current averaged over a complete cycle to be different from zero and a negative bias condition is achieved at the cathode. The negative dc potential on the target surface repels electrons from the vicinity of the surface creating a sheath enriched in ions in
front of the target and the sputtering is achieved. A 13.56 MHz frequency is
generally used for rf sputtering as this frequency is reserved for plasma processing
by the Federal Communications Commissions. One of the important aspects in rf
sputtering system is the impedance matching network between power supply and
discharge chamber. This network consists of an LC circuit with variable
impedance. The impedance is matched between the power supply and load (in this
case plasma), by varying the impedance of this network to transfer maximum
power to the load. Also, adequate grounding of the substrate assembly must be
ensured to avoid undesirable rf voltages, which can develop on the surface. Since
capacitive reactance is inversely proportional to the capacitance or area, more
voltage will be dropped across the capacitor of a smaller surface area. Therefore,
for efficient sputtering, the area of the target electrode should be small compared to
the area of the anode. This condition is satisfied by making bigger substrate
platform (effective electrode) as compared to cathode.

In order to make thin films of compounds like oxides, nitrides and carbides,
reactive sputtering technique is used. In this method, the sputtered atoms or ions
react with the reactive gas and form compounds, which get deposited on the
substrates. High activation energy needed for chemical reaction requires the
presence of ionized atoms or plasma.
2.1.2 Description of sputtering unit

A rf sputtering unit has been indigenously developed [1] at NSC for depositing different thin films. The schematic of the coating unit is given in figure 2.1. This consists of three parts: sputtering chamber and the vacuum system, the gas flow system and the rf system with matching network.

![Schematic diagram of rf sputtering set up](image)

Figure 2.1: Schematic diagram of rf sputtering set up
Chapter 2: Materials under study and their development

The sputtering chamber is made of stainless steel having a diameter of 40 cm. It contains a target holder acting as cathode (10 cm diameter) and a substrate holder acting as anode. Substrates are kept on the anode at a distance of 5 cm from the cathode. This distance is chosen in a manner such that enough number of collisions should take place in the gaseous medium for an operating pressure ($\sim 5 \times 10^{-2}$ Torr to $7 \times 10^{-2}$ Torr). The cathode is connected to the rf power supply. The anode and the rest of the system are properly grounded with metallic strips. The substrate holder is kept on an electrically insulated height adjustable table. It is attached to a heating coil, which acts as the substrate heater. This is connected to a variac to change current in the heater and hence the temperature. A thermocouple based temperature sensing is used to read the temperature. A temperature controller is used to stabilize the substrate temperature within few degrees. A schematic diagram of inside view of the chamber is given in figure 2.2. To evacuate this chamber, a diffusion pump (500 l/s) based high vacuum system is used. A rotary pump (200 l/min) is used for backing the diffusion pump as well as to rough the sputtering chamber. An ultimate base pressure of $2 \times 10^{-6}$ Torr is obtained. The target holder is a metal holder fitted with a teflon ring. The metal holder has water connections in order to cool the target. The teflon ring contains circular rubber gasket which is fitted into the grooves of the ring. To the scale diagrams of the target holder and teflon ring are shown in figure 2.3. A proper rf shielding is made in the sides of cathode (as shown
in figure 2.2) to check the spread of plasma in unwanted direction inside the chamber and to maximize the plasma within cathode and anode.
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Figure 2.3: To the scale diagrams of target holder and teflon ring
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The gas flow system consists of two mass flow controllers (MFC) and the MKS 4-channel read out. The MKS flow meter with controller accurately measures and controls the mass flow rate of gases. Upon entering the flow meter or controller, the gas streams are divided into two parallel paths. The first is directed to the sensor tube and the second through the control valve before exiting the instrument. The unit of gas flow is in standard cm³ min⁻¹ (sccm).

The rf assembly has been designed and fabricated at NSC. RF system essentially consists of two parts, rf amplifier with power supply and impedance matching network. The rf amplifier is a crystal controlled C type amplifier. The maximum power that can be delivered to the load from this rf power supply is 500 W. The matching network consists of two tunable capacitors and a fixed inductor. Matching network is configured with self tuning circuits, which adjust the level of the two capacitors to find the best impedance match.

2.1.3 Deposition of Cu₃N, Cu₂O and CuO films

Three Cu₃N films are prepared on borosilicate glass substrate [2] by the above described rf sputtering system. The target is a copper disc of 10 cm in diameter and has purity of 99.999%. After achieving an ultimate base pressure of 2x10⁻⁶ Torr, high purity nitrogen gas is introduced in the chamber. Gas flow, through the mass flow controller is 15 sccm. RF power is capacitively coupled to the cathode and the power applied to the cathode is about 100 W. During deposition, the high vacuum
valve remains closed and the process pressure is kept about $5 \times 10^{-2}$ Torr using the rotary pump only. Films are deposited in the nitrogen plasma environment in three runs. Before deposition, Cu target is pre sputtered by nitrogen plasma to clean the surface. During deposition, substrate temperature is kept at 30 °C (no deliberate heating of the substrate), 75 °C and 150 °C in the first, second and third runs respectively. Deposition time for each run is kept about 15 min. Brown colored, transparent thin films are deposited on the glass substrate. The films are named as 1-A, 1-B and 1-C corresponding to substrate temperature 30 °C, 75 °C and 150 °C, respectively.

Cu$_2$O and CuO films are deposited on borosilicate glass substrate [3] by the same sputtering unit as discussed in the previous section. In this case, after achieving the ultimate base pressure, high purity oxygen gas is introduced in the chamber with a flow rate of 7.5 sccm using MKS flow controller. The rf power is kept about 200 W. During deposition, substrate temperature is kept at 30 °C (no deliberate heating of the substrate), 150 °C and 300 °C, respectively. Process pressure is $5 \times 10^{-2}$ Torr. Deposition time for each film is kept about 15 min. Brownish-black colored transparent films are deposited on the substrate. The films are named as 2-A, 2-B and 2-C corresponding to substrate temperature 30 °C, 150 °C and 300 °C, respectively.
2.2 Vacuum evaporation technique and deposition of SiO$_2$, a-C and C$_{60}$ films

Films of SiO$_2$, a-C and C$_{60}$ are deposited by vacuum evaporation method in high vacuum deposition chamber at the target deposition laboratory, NSC. Films of a-C and SiO$_2$ are deposited by electron beam evaporation technique whereas C$_{60}$ films are deposited by resistive heating method. In this section, first a brief description of vacuum evaporation methods will be made, followed by deposition of these films.

2.2.1 Vacuum evaporation method

This is a standard technique of thin film deposition in a high vacuum environment. A sufficient amount of heat, in a vacuum environment, given to the evaporant which provides the necessary vapor pressure for evaporation. When evaporation is made in vacuum, the evaporation temperature is considerably lowered and the formation of oxides and the incorporation of impurities in the growing layer is reduced. The rate of deposition of any vapor on a substrate depends upon the source geometry, the position of the source relative to the substrate, and the condensation coefficient.

Vacuum evaporation can be done in two ways: electron beam bombardment and resistive heating. In the electron beam evaporation method, the vaporization of materials is accomplished by electron bombardment. A stream of electrons is
accelerated through about 5 – 10 kV and focussed onto the surface of the material for evaporation. Typical current is up to ~ 500 mA. The electrons lose their energy very rapidly upon striking the surface, and the materials melt at the surface and evaporate. The rate of evaporation varies from fraction of an Å per seconds to hundreds of Å per second. Schematic of the high vacuum evaporation chamber is shown in figure 2.4.

Figure 2.4: Schematic diagram of high vacuum deposition chamber.
In resistive heating method, the temperature of evaporant is kept on a filament or boat made up of refractory metal (Ta, Mo, W etc.). The filament is heated by passing current in it. The evaporant attached to it gets melted and then evaporated.

2.2.2 Deposition of SiO$_2$ film

SiO$_2$ films have been deposited on copper substrate by electron beam evaporation technique in ultra high vacuum (UHV) environment ($\sim 3.7 \times 10^{-8}$ Torr). A pellet is made from the powder of SiO$_2$ and evaporation of this pellet is performed by heating it with electron beam of $\sim 80$ mA current. Films are deposited on the substrate kept at a distance of $\sim 20$ cm and named as 2-D.

2.2.3 Deposition of a-C film

Films of a-C are deposited on silicon substrate by electron beam evaporation method in high vacuum environment ($2 \times 10^{-6}$ Torr). A graphite pellet is kept in the hearth of the electron gun. Electron beam is generated by passing current of $\sim 100$ mA in the filament. The electron beam hits the pellet and vaporizes it. Vaporized carbon gets stuck to the substrate kept normally above the hearth at a distance of $\sim 20$ cm. Films are named as 3-A.

2.2.4 Deposition of C$_{60}$ film

Fullerene films of different thickness (18 nm, 30 nm, 100 nm, 170 nm and 250 nm) are deposited on Si substrate. One film of thickness 18 nm is deposited on borosilicate glass substrate. Resistive heating method is used for deposition of these films. Commercially available C$_{60}$ powder is palletized and is used for this film
deposition. Evaporation is done at a rate \( \sim 0.1 \text{ nm/s} \) by passing a current of \( \sim 75 \text{ A} \) in a Ta boat. The deposition is done in high vacuum (\( 2 \times 10^{-6} \text{ Torr} \)) environment.

These films are named as 3-B1, 3-B2, 3-B3, 3-B4, 3-B5 corresponding to thickness of 18 nm, 30 nm, 100 nm, 170 nm and 250 nm, respectively and 3-B6 corresponding to the film (18 nm) deposited on glass substrate.

2.3 Magnetron sputtering technique and deposition of a-C:H films

Films of a-C:H are grown by unbalanced magnetron sputtering technique [4] at Gintic Institute of Technology, Singapore. In this section an introduction of magnetron sputtering technique will be given, followed by the deposition of the a-C:H films in brief.

2.3.1 RF magnetron sputtering

The magnetron sputtering is a simple and reliable process, which is now currently used for industrial deposition of thin film coatings. This is a modification over simple rf sputtering for higher deposition rate at low pressure. In the low pressure (typically below \( 1 \times 10^{-2} \text{ Torr} \)), electrons escape from the active region due to random collisions and hence the glow stops. This problem can be tackled by an improvement of the plasma confinement. If a magnetic field is applied parallel to the rf field, it will constrain the electrons to move within the electrodes and the efficiency of the rf glow discharges improves due to the electron confinement [5].
2.3.2 Deposition of a-C:H films

Films of a-C:H are deposited on silicon substrate in the deposition set up of Teer Coatings, Inc. UK. The schematic of the deposition set up is given in figure 2.5.

![Schematic diagram of rf magnetron sputtering set up.](image)

The base pressure obtained in the sputtering chamber is below $6.7 \times 10^{-8}$ Torr, and the working pressure is $8.5 \times 10^{-3}$ Torr during deposition. The substrate is placed in a rotary sample holder facing the rectangular graphite target (99.9 %, GfE Gesellschaft für Elektrometallurgie MBH, Germany) 33 cm × 13.3 cm in size,
situated 8.5 cm above the sample. The power to the magnetron target is supplied from the MDX magnetron drive from Advanced Energy Industries Inc., USA. Substrate is biased by 13.56 MHz rf supply (RFXII 1250) to eliminate charge accumulation during deposition. The graphite target is sputtered at different hydrogen gas flow rate (up to 20 sccm) and a-C:H coatings are deposited. Total six films are used under study. These are named as 3-C, 3-D, 3-E, 3-F and 3-G.

2.4 Hot filament chemical vapor deposition (HFCVD) technique and deposition of diamond film

Diamond films have been grown by hot filament chemical vapour deposition (HFCVD) technique [6] at Department of Physics, IIT, Bombay. In this section, a brief introduction on HFCVD technique will be given first and then the deposition of diamond film will be described.

2.4.1 HFCVD technique

It is one of the versatile methods used for the low-pressure synthesis of diamond on non-diamond substrates. In this deposition the source gases interact with a hot surface, usually a thin wire of refractory carbide or metal. Source gases are typically methane or other hydrocarbons. The hot filament decomposes the source gases, forming hydrocarbon free atomic radicals and atomic hydrogen. These active species diffuse to the substrate where diamond is formed. Pressure range from a few to several hundred Torr, substrate temperature from 800 to 1100°C, and filament temperatures from 2000 to 2600°C.
2.4.2 Deposition of diamond film

Diamond films are deposited on silicon substrate by HFCVD technique. Schematic of the deposition set up is given in figure 2.6.

A high current low voltage ac transformer is used for heating a tungsten filament. CH\(_4\) with volume percentage of 0.8% and rest H\(_2\) is used as a precursor gas. The
flow rate of the gases is measured using mass flow controllers. The temperature of the substrate (Si<100> wafer) is measured using a thermocouple. The temperature of the filament in HFCVD is measured using an optical pyrometer. The substrate temperature is fixed at 925°C. The growth pressure is kept at 20 Torr. This film is named as 3-H.

Graphite sample is procured ESPI, USA and named as 3-I.

In the table below, the deposition techniques and corresponding nomenclature of the films are given:

**Table 2.1**

<table>
<thead>
<tr>
<th>Deposition technique</th>
<th>Name of the samples</th>
<th>Substrate</th>
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<td>Borosilicate glass (Copper nitrides)</td>
</tr>
<tr>
<td></td>
<td>2-A, 2-B and 2-C</td>
<td>Borosilicate glass (Copper oxides)</td>
</tr>
<tr>
<td>Electron beam evaporation</td>
<td>2-D (SiO₂)</td>
<td>Si (100)</td>
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<td></td>
<td>3-A (a-C)</td>
<td>Si (100)</td>
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<tr>
<td></td>
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<td>Si (100)</td>
</tr>
<tr>
<td></td>
<td>3-B6 (C₆₀)</td>
<td>Borosilicate glass</td>
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<tr>
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<tr>
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<td>3-H (diamond)</td>
<td>Si (100)</td>
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Bibliography


