PH401 – Introduction to Nanomaterials

End-Semester Examination

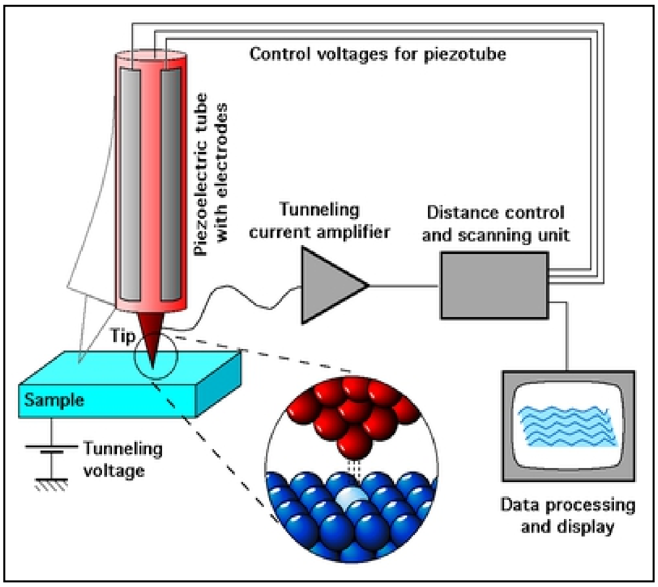
Name: **M Maheeth Reddy**	Roll No.: **1801CS31**	Date: **22-Nov-2021**

Ans 1:

Discuss the working principle of STM. What are modifications needed to be taken care of by an engineer to image the semiconductor materials (thin films) by using the STM? Can one get magnetic domain distribution by using STM? Justify your answer.

The Scanning Tunneling Microscope (STM) works by scanning a very sharp metal wire tip over a surface. By bringing the tip very close to the surface, and by applying an electrical voltage to the tip or sample, we can image the surface at an extremely small scale – down to resolving individual atoms.

- The basic principle of STM is Tunneling. It is a quantum mechanical effect. A tunneling current occurs when electrons move through a barrier that they classically shouldn't be able to move through. In classical terms, if you don't have enough energy to move "over" a barrier, you won't.
- Tunneling current flows between tip and sample when separated by less than 100nm
- The tunneling current gives us atomic information about the surface as the tip scans

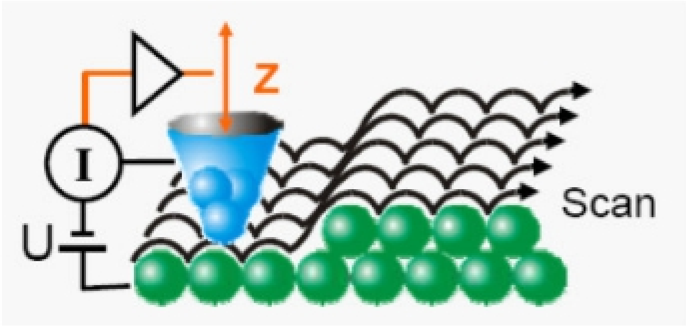


A Setup of Scanning Tunneling Microscope

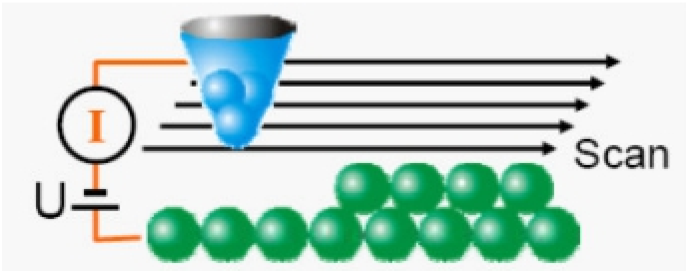
Modifications to STM for imaging semiconductor materials (thin films)

Two modifications can be done to image semiconductors:

1. **I constant, feedback loop active, Z variation measured** (preferred)

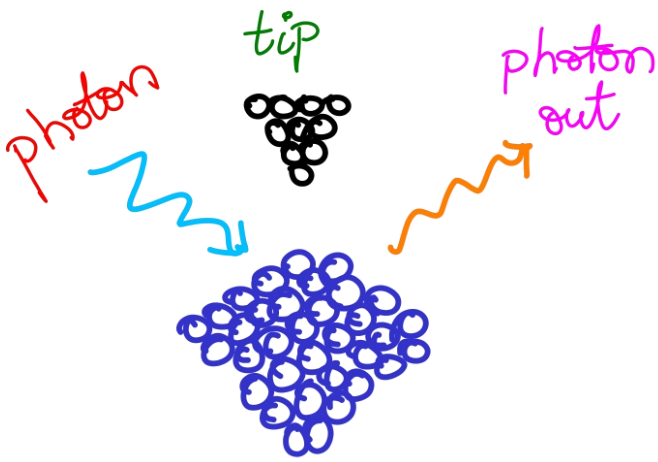


2. **Z constant, feedback loop idle, I variation measured**



However, STM alone cannot address questions regarding the optoelectronic processes that can occur at the interface. To overcome the limitation, innovative STM strategies, which allow optical imaging and manipulation of light below the diffraction limit.

For Nanomaterials,



No, we cannot obtain magnetic domains with STM. Instead we can use the following methods for observation:

- Magnetic Force Microscopy (MFM)
- Magneto Optical

Ans 2:

Prove that the angle between the armchair and zigzag chiral vector is 30^0. Calculate the angle of helicity and diameter of (4,12), (3,13), (18,18), and (14,0) carbon nanotube, and mention their nature of electrical conduction.

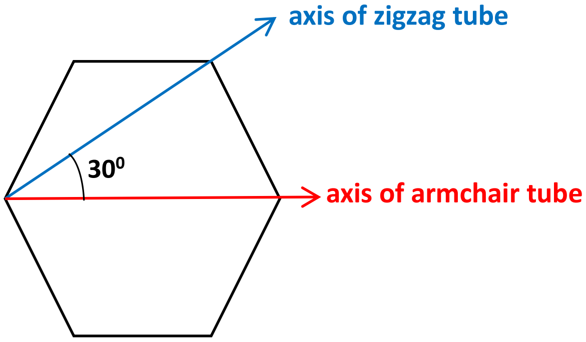
Proof: Angle between the armchair and zigzag chiral vector is 30^0

The rolling of graphene sheets can be done in several ways. Each way of rolling will result in different translational vectors pointing in separate directions.

In the **zigzag tube**, the graphene hexagons point along the long axis of the tube.

In the **armchair tube**, the flat side of the hexagon lies along the long axis of the tube.

In the **chiral nanotube**, the configuration lies between the above two mentioned extremes. This can be depicted in the diagram shown below.



So, the maximum angle between the translational vectors of the zigzag and the armchair nanotubes is always 30^0, as depicted in this diagram

To find the angle of helicity and diameter fo the **four** configurations of nano-tubes given, the following formulae can be used:

Angle of Helicity, $\theta = \sin^{-1}\frac{\sqrt{3}m}{2\sqrt{n^2+nm+m^2}}$

Diameter, $D = \frac{|C_h|}{\pi} = \frac{a_{CC}\sqrt{3(n^2+nm+m^2)}}{\pi}$, where 1.41Å (graphite) ≤ $a_{C=C}$ ≤ 1.44Å (C_{60})

The **Electrical Conductivity** of a carbon nanotube can be determined by **checking whether the value of (n-m) is a multiple of 3**

I have tabularized the properties of each nanotube as shown below:

Nanotubes	Diameter (in nm) $A_{C=C}$ = 1.41A	Angle of helicity (degrees)	Difference of n,m	Electrical Conductivity
(4, 12)	1.121	46.1	8	Semi-Conducting
(3, 13)	1.145	49.83	10	Semi-Conducting
(18, 18)	2.42	30	0	Yes
(14, 0)	1.088	0	14	Semi-Conducting

Ans 3:

An engineer got the XRD pattern of steel noted the following data (Table in the answer below). Identify the peaks that correspond to carbon and iron. Find the crystallite size of carbon and iron in the composite. Assume 4% carbon is added to the iron matrix.

Given: XRD Pattern for steel with 4% carbon added to the iron matrix.
From the given data it is evident that the composite is a Medium Carbon Steel with FCC crystal structure.

We can calculate the Average Crystalline Size (D) using the Scherrer's formula below:

$$\mathrm{D} = \frac{k\lambda}{FWHM \times cos\theta}$$

where,
k is 0.94 for a circular grain
λ is the Wavelength of the X-Ray (1.54 Å)
FWHM is the Full Width Half Maximum of the peak, in radians
θ is the diffraction angle
Putting values in the above equation we get the crystallite sizes for the given data as:

2θ (deg)	Intensity (CPS)	FWHM (deg)	Average Crystalline Size D (nm)
26.53	100	0.237	**35.95**
44.58	900	0.345	**25.97**
55	40	0.421	**22.20**
64.98	152	0.332	**29.61**
82.29	332	0.384	**28.68**

Thus, from the above data we can interpret that the peak with Intensity of 40 CPS corresponds to Carbon and the peak with 100 CPS corresponds to Iron.

From the table above, we can deduce that the crystallite size of Carbon in the composite is 22.20nm and the crystallize size of Iron is 35.95nm

Ans 4:

A company has asked an engineer to make a design and specification of a magnetic lens for a 200KV TEM machine. Discuss the design of the magnetic lens for the 200KV TEM machine. Plot focal length versus current (in the coil) which will help the mechanic to make the lens as well as it will help the operator for imaging.

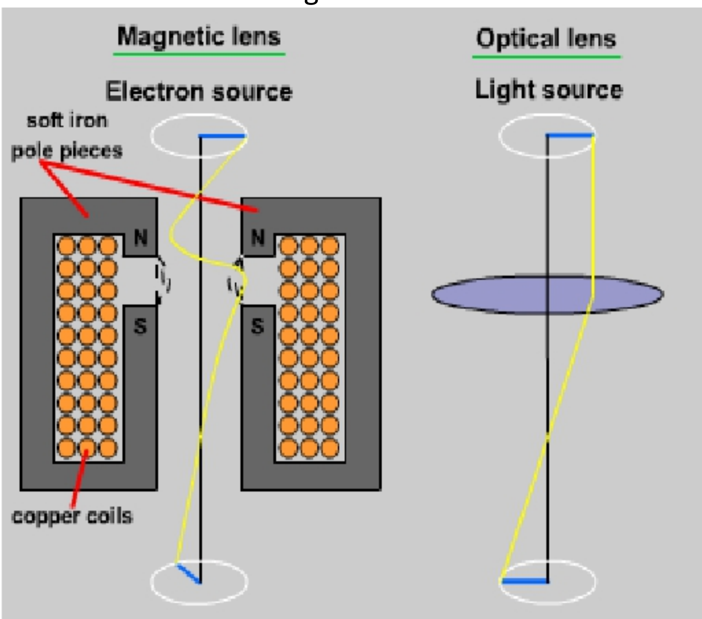
Magnetic Lens

A magnetic lens is a device for the focusing or deflection of moving charged particles, such as electrons or ions, by use of the magnetic Lorentz force. Its strength can often be varied by the usage of electromagnets. They are prominently used in cathode ray tubes, electron microscopy, particle accelerators etc.

In classical microscopes, whatever is observed by the naked eye is treated as observation. Due to this, the errors in observation are comparatively less significant. But in nanomaterials or nanoscience, there is a need for high accuracy. Even an error of the order of nanometers is considered a significant error. This is the reason why magnetic lenses are used in Transmission Electron Microscopes (TEMs). Magnetic Lenses can precisely control the flow of the electrons emitted by the electron gun in a TEM, which is important for getting a precise output. Hence, the design of a magnetic lens for a TEM is of high importance.

Design of Magnetic Lens:

1. The magnetic lens consists of a tightly wound coil and a soft iron shroud surrounding the coil except for a small gap. The field is concentrated in that gap.
2. The magnetic field generated through the coil will act as a lens and would converge the electron on the sample to form an image.
   This is similar to an optical lens in which electromagnetic radiation is the source instead of electrons and an optical lens will converge the radiation towards the focal length of the lens and an image is formed.



3. The Magnetic lenses used in TEMs are always constructed with an iron circuit to produce a high field strength across a short gap.
4. The magnetic fields for TEM lenses are in the range of 10,000 - 20,000 gauss.
5. The focal length for the magnetic lens could be calculated using the formula below:

$$\mathbf{f} = \frac{K.V_r}{(N.I)^2}$$

Where,
f is the focal length of the magnetic lens,
K is the engineering constant, a constant that is dependent on the dimensions and environment of the setup (determined experimentally),
V_r is the accelerating voltage and is given to be 200KV,
N is the number of turns in the excitation coils, and I represents current

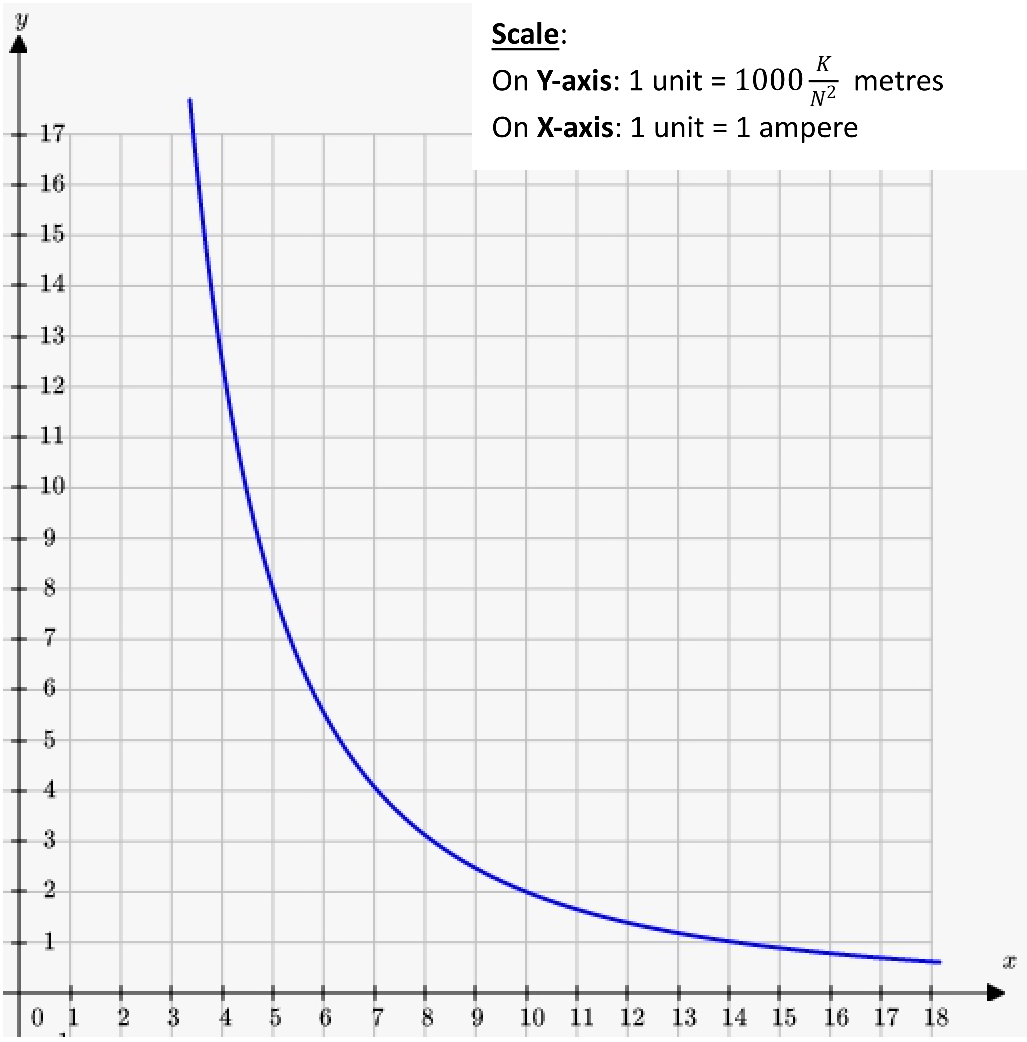
A new TEM must be calibrated first before it is used to take micrographs or diffraction patterns.

As evident from the formula, the focal length of the magnetic lens can be altered by changing the strength of the current.

Plotting focal length vs. current

In the above formula for focal length, only V_r is known to be 200KV. Other parameters like K and N depend on the TEM setup. Hence, I have plotted the focal length in terms of K and V in the following manner.

$$\mathbf{f} = \frac{10^3 \times K}{N^2} \times \frac{200}{\mathbf{I}^2}$$



Scale:

On **Y-axis**: 1 unit = $1000\frac{K}{N^2}$ metres

On **X-axis**: 1 unit = 1 ampere

Focal Length is on Y-axis, in terms of K, N and Current I is on X-axis in amperes.

How will the above graph help the operator for imaging?

From the formula stated above, it is clear that focal length depends on strength of current. So, the changes in current will affect the focal length. By using the above graph, the operator will be able to determine the correct strength of the current to focus the specimen properly.

Underfocusing the specimen may lead to the formation of a bright ring around the image. Overfocusing the specimen may lead to a dark ring forming around the image. So, the operator needs this graph to deterimne the right focal length of the magnetic lens to properly focus on the specimen and avoid any rings in the magnified image.

Ans 5:

No electromagnetic radiation is used in AFM for imaging. Justify the statement. In AFM technique, one measures the force between AFM tip and sample forces. What kinds of forces can be measured here? How many minimum number of detectors (not the photodiode alone complete detector) are required in AFM for imaging? Justify your answer. Discuss the working principle of detectors in AFM.

No electromagnetic radiation is used in Atomic Force Microscopy (AFM) because only the atomic forces are considered. Electromagnetic radiation is not used while measuring the micrograph or atomic surface of the sample.

Principle of Atomic Force Microscopy

- The tip of the probe of the atomic force microscope is brought very close to the sample such that they are seperated by a distance in the atomic range.
- Because of this positioning, the sample and the tip will experience atomic forces and this helps to determine the depths at various parts.

So, clearly electromagnetic radiations are not at all used in AFM. The closer the tip of the AFM's probe is to the surface, the greater is the force experienced and the farther they are, the lesser the force. This is how the profile is thus generated.

The different kinds of forces that can be measured are:

1) Vanderwaals forces
2) Electric forces
3) Magnetic forces
4) Torsional resistance
5) Capacitance
6) Conductive atomic forces.

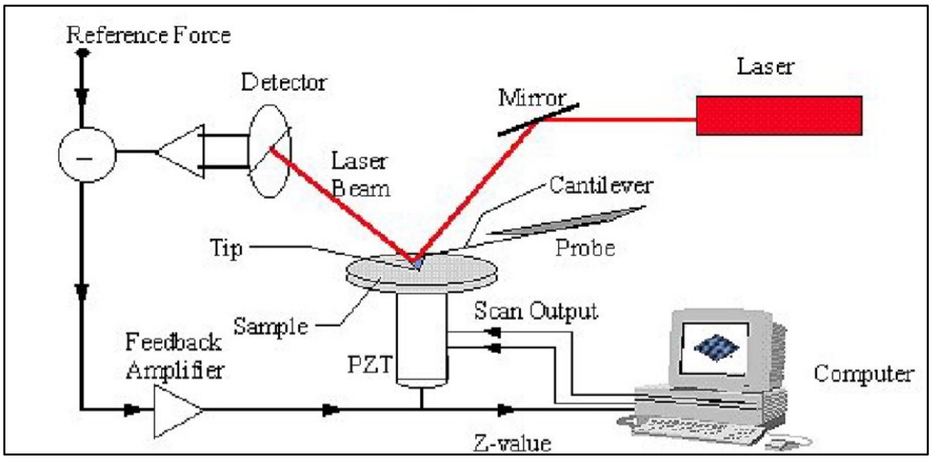
The minimum detectors that are required in the AFM for imaging are:

1) Photo-diode
2) Feedback Voltage

Working Principle of detectors in AFM

The surface profile can be measured in 2 ways inside the AFM:

1. by keeping the current constant inside the photo-diode or,
2. by keeping the distance between the probe and the surface constant.



Experimental Setup of Atomic Force Microscopy

In the experimental setup for AFM, there is a laser which strikes the mirror and reflected from the tip which is moving over the surface. The reflected beam is then incident on the photodiode detector which measures the current, and the feedback amplifier gives the voltage between the sample and the tip.

Scenario 1:

So, if the distance between the tip and surface needs to be constant, the voltage is kept constant since the distance depends on the voltage. Now, if the distance is constant, the tip goes up and down depending on the surface profile, since the surface is not smooth at nano scale, and hence it deflects so the laser beam which reflects from tip also changes and the current changes on the photo-diode is recorded.

Scenario 2:

But if the tip should be moving at the same line and should not deflect voltage needs to be changed such that it does not deflect and moves in a particular straight motion. So It does not deflect and reflected light beam is totally constant and there is constant current detection. But here the surface is detected by voltage.

So, the surface can be detected either by changing the voltage or detecting the changing current either one of them.

Ans 6:

A particulate composite is made up of Fe and Co metals ($Fe_{1-x}Co_x$). The x varies from 0 to 1 as follows: x = 0, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.92, 0.94, 0.96, 0.98, 1.0. Plot the tensile strength, Young modulus and magnetic moment per formula unit in μ_B versus composition of Fe and Co. The average crystallite size of both Fe and Co is 40nm. [Tensile strength of Fe = 540 MPa and Co = 800 MPa, Young modulus of Fe = 211 GPa and Co = 209 GPa, magnetic moment per formula unit of Fe = 2.7 μ_B and Co = 2.3 μ_B].

Given, Nano-composite is $Fe_{1-x}Co_x$.

Let us assume there are (a+b) moles of the nano-composite, such that there are a moles of Fe and b moles of Co. Therefore,

$$\frac{b}{a+b} = x$$

$$\frac{a}{a+b} = 1 - x$$

Consider Fe,

$$\mathrm{a} = \frac{\mathrm{W_{Fe}}}{\mathrm{M_{Fe}}}$$

$$\Rightarrow \mathrm{a} = \frac{\rho_{\mathrm{Fe}}\mathrm{V_{Fe}}}{\mathrm{M_{Fe}}}$$

$$\Rightarrow \mathrm{V_{Fe}} = \frac{\mathrm{a\,M_{Fe}}}{\rho_{\mathrm{Fe}}}$$

W is Total Weight
M is Molecular Mass

$$\frac{Mass}{Volume} = Density$$

Similarly for Co,

$$\mathrm{V_{Co}} = \frac{\mathrm{b\,M_{Co}}}{\rho_{\mathrm{Co}}}$$

Determining the volume fractions, VF

$$VF_{Fe} = \frac{V_{Fe}}{V_{Fe} + V_{Co}} = \frac{a\,M_{Fe}\,\rho_{Co}}{a\,M_{Fe}\,\rho_{Co} + b\,M_{Co}\,\rho_{Fe}}$$

On dividing numerator and denominator by (a+b),

$$VF_{Fe} = \frac{(1-x)\,M_{Fe}\,\rho_{Co}}{(1-x)\,M_{Fe}\,\rho_{Co} + x\,M_{Co}\,\rho_{Fe}}$$

As $\mathrm{VF_{Fe}} + \mathrm{VF_{Co}} = 1$

$$VF_{Co} = \frac{x\,M_{Co}\,\rho_{Fe}}{(1-x)\,M_{Fe}\,\rho_{Co} + x\,M_{Co}\,\rho_{Fe}}$$

For nanoparticles we know that

a) Tensile Strength (σ_{eff})

$$\sigma_{\mathrm{eff}} = \frac{\sigma_{\mathrm{Fe}}\sigma_{\mathrm{Co}}}{\sigma_{\mathrm{Fe}}\mathrm{VF_{Co}} + \sigma_{\mathrm{Co}}\mathrm{VF_{Fe}}}$$

b) Young's Modulus (Y_{eff})

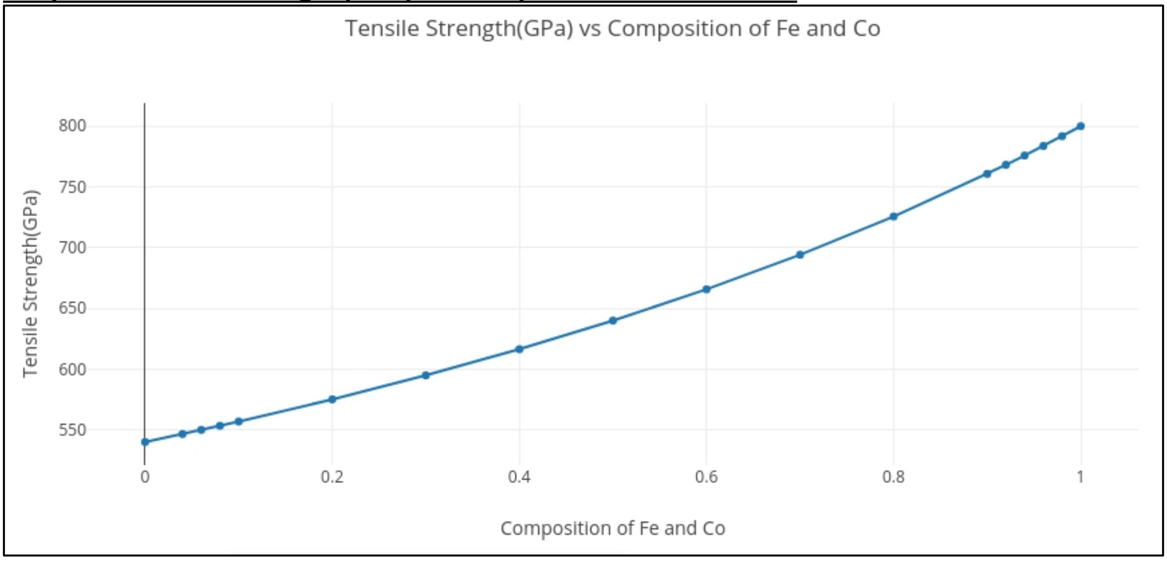
$$Y_{eff} = \frac{Y_{Fe}Y_{Co}}{Y_{Fe}VF_{Co} + Y_{Co}VF_{Fe}}$$

c) Magnetic Moment (M_{eff})

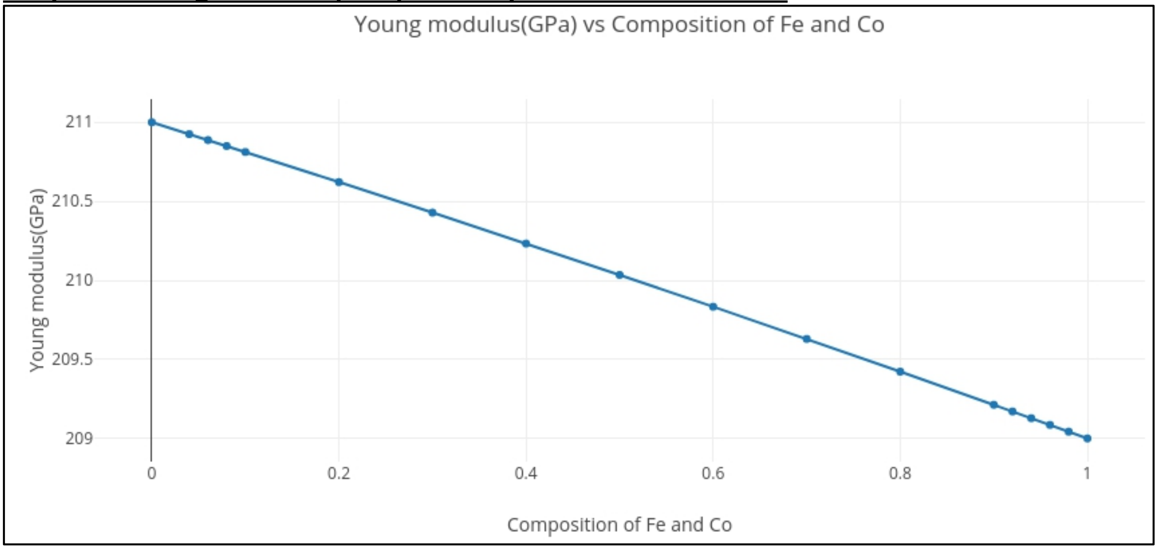
$$M_{eff} = \frac{M_{Fe}M_{Co}}{M_{Fe}VF_{Co} + M_{Co}VF_{Fe}}$$

Substituting the given values:
σ_{Fe} = 540MPa, σ_{Co} = 800MPa,
Y_{Fe} = 211GPa, Y_{Co} = 209GPa,
$\mu_{Fe} = 2.7\mu_B$, $\mu_{Co} = 2.3\mu_B$,
M_{Fe} = 55.85u, M_{Co} = 58.93u,
$\rho_{Fe} = 7.8\text{x}10^3$ kg/m^3, $\rho_{Co} = 8.9\text{x}10^3$ kg/m^3

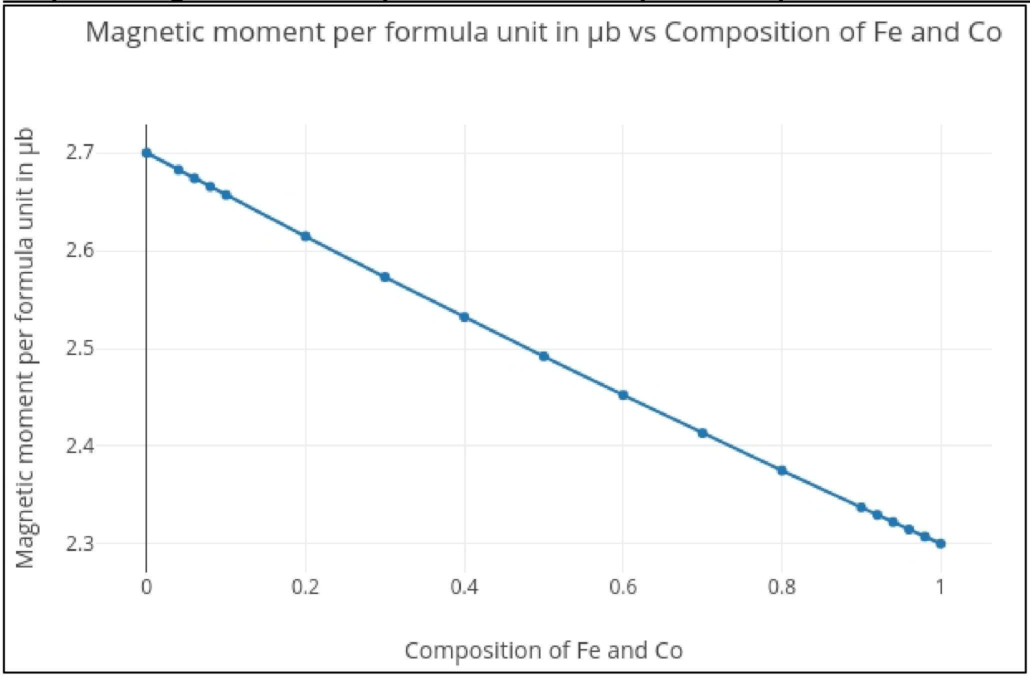
Graph of Tensile Strength(GPa) vs Composition of Fe and Co:



Graph of Young modulus(GPa) vs Composition of Fe and Co:



Graph of Magnetic Moment per formula unit in µB vs Composition of Fe and Co:



Ans 7:

What are the advantage and disadvantages between magnetic (magnetic memory device) and magnetoresistive (magnetoresistive memory device) recording media?

Magnetic Memory Devices:

Magnetic Memory Devices are the storage devices which capture and store data on a magnetized medium. They use different forms of magnetization patterns in a magnetizable material for permanent storage of information.

They possess a non-volatile memory where the information is accessed using read and write heads containing electromagnets to create magnetic charges on the medium. The data gets stored with the rotation of the medium.

Examples: Diskettes, Hard Disks, Floppy Disks, Disk Cartridges, Magnetic Tapes

Advantages of Magnetic Memory Devices

1. Capable of storing large amounts of data - upto 1 Terabyte per tape cartridge
2. Data is not lost when the computer is switched off
3. Cheap form of data storage
4. Less cumbersome than multiple optical disks
5. Greater speed of processing and accessing data
6. They can store huge data in less space
7. They are considered to be the best secondary storage devices as they are cheaper and lighter in weight and non-volatile in nature

Disadvantages of Magnetic Memory Devices

1. Serial access can be quite slow to access data.
2. They consume very high amount of electric power.
3. Data may be corrupted if the tape is placed near a magnetic field like a large speaker.

4. Need a special piece of equipment to record and read the data on the tape.
5. These devices easily deteriorate over time.
6. They have slower processing speed as compared to SSDs.

Magnetoresistive Memory devices:

Magnetoresistive memory devices are a type of non-volatile random-access memory which stores data in magnetic domains. It mainly includes the magneto resistive random access memory(MRAM). Unlike conventional RAM chip technologies which use electric charge or current flows for data storage, MRAM uses magnetic storage elements. The elements are formed from two ferromagnetic plates, each of which can hold a magnetization, separated by a thin insulating layer. The bottom layers give an effect of fixed (pinned) layer due to interlayer exchange coupling between ferromagnetic and spacer layer of synthetic antiferromagnetic.

Advantages of Magnetoresistive Memory Devices

1. They are non-volatile hence data storage is permanent
2. Infinite endurance and do not damage easily
3. Possess a high speed performance.
4. Available at low cost
5. More Compactness due to the use of nanomaterials
6. Greater Reliability due to the use of nanomaterials

Disadvantages of Magnetoresistive Memory Devices

1. Has first generation selectivity and scalability problems.
2. Memory technology is not scalable at the 32 nm node.
3. The magnetization of nanomaterials is flipped back and forth because these devices utilize heavily spin polarized current and there is no applied magnetic field.
4. Heating Issue due to above mentioned magnetic switching
5. Instability issues
6. Write failure and data erasure problems

Ans 8:

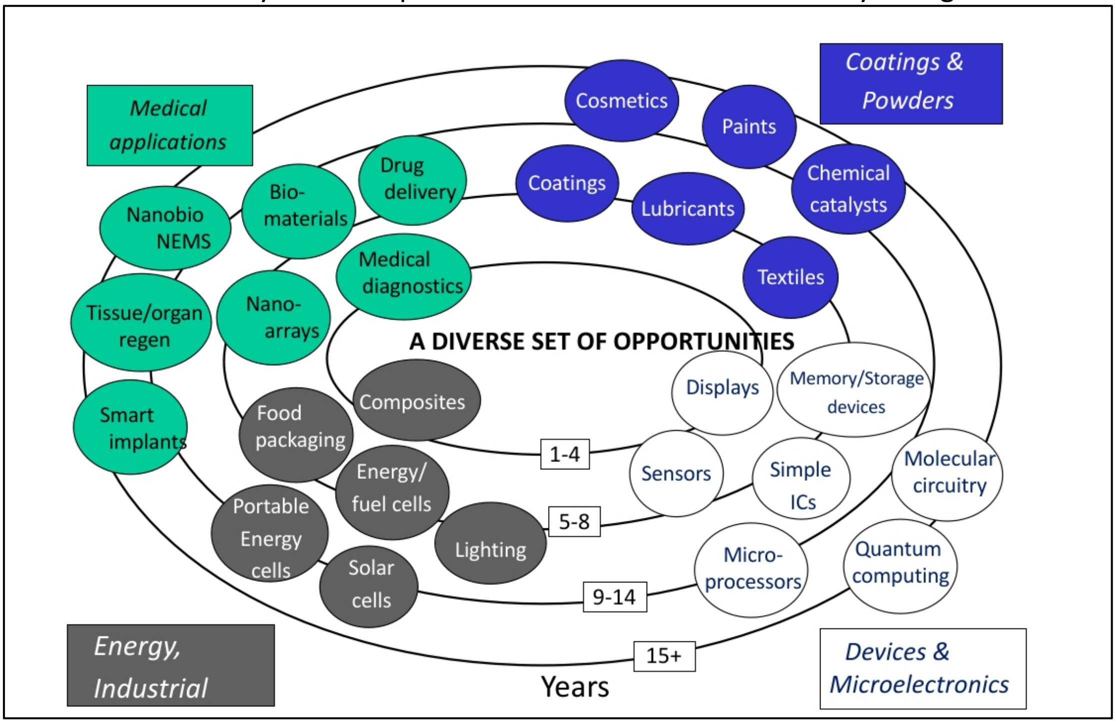
What is/are the most important information/s you learn from this course?

I heard the terms Nanomaterials and Nanotechnology quite a few times before enrolling in this course, mostly like a technical jargon. But I never knew the meaning of Nanomaterials in its true sense. Before I enrolled in this course, the only thing that came to my mind is Iron Man from the Avengers movies (adjacent picture).

So when I had the chance to know more about nanotechnology through this course, I grabbed the opportunity and I am glad it was worth it.

I have learnt a lot of information from this course. I have listed the topics I learnt in brief, in the following manner:

- Definition of Nanotechnology: Nanotechnology is the study of functional structures with dimensions in the 1-100nm range, in at least one dimension, to achieve size depended properties and functions
- History of Nanomaterials: Ochre Pigments, Maya Blue, Lycurgus Cup, Damascus Sword etc. We also looked at the **timeline of the discoveries** related to nanomaterials
- Few Concepts about Nanomaterials like Non-reflective surfaces, Self-Cleaning, Super-Hydro Phobicity, Surface Plasmon Resonance
- Synthesis of Nanomaterials (based on Quantum Effect):
  - **Top-Down Methods** like Ball Milling, Rolling and Beating, Annealing Gas Atomization, Lithographic Methods etc.
  - **Bottom-Up Methods** like CVD, Atomic Layer Deposition, Liquid Phase Bottom-up methods, Bottom-Up Lithographic Methods etc.
  - Other methods that are **combination of both Top-Down and Bottom-Up**
- Applications of Nanotechnology:
  - In Medicine:
    - Detection add Treatment of Cancer
    - In Magnetic Resonane Imaging (MRI)
    - Immunoassays
    - RNA & DNA purification
  - In Electron Microscopy like SEM, TEM
  - In the fabrication of Data Storage devices
  - Synthesis of Carbon Nanotubes
- There is a long list of other potential applications of nanotechnology. So, I have taken the liberty to take a picture which better summarizes my thoughts.



The Various fields where Nanomaterials has potential applications

The development of the field of Nanotechnology is something to watch out and its potential contribution to future of technology in general is an exciting aspect. I am looking forward to the day when the word "Nanotechnology" will not be a technical jargon for a majority of the population.

"I hope there would be one day in the distant future when the Iron Man suit in the picture above is no longer just science fiction stuff."

THE END