ESTIMATION OF PLASMA FREQUENCY OF CERTAIN METAL THIN FILMS PREPARED BY DC MAGNETRON SPUTTERING

Report of Summer Project done

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Estimation of Plasma Frequency of Certain Metal Thin Films Prepared by DC Magnetron Sputtering

1 Introduction

For a long time, for most of our information transfer uses, we used electronics, which depended on the motion of electrons, or electricity. As technology advanced, electronic devices became smaller and smaller until they reached the nanoscale, which was one of the many benefits of electronics. However, we sought faster processing speeds, which is why we turned to the use of light, or the field of photonics. Using and controlling photons or light for information transfer did allow much faster communication compared to electronics, but it had its own problem. Unlike electronic devices, photonic devices can't be made smaller than a certain size because of the diffraction limit of light [1]. That is, only devices that have sizes comparable to that of the wavelength of a particular light can be used to control or direct it, which severely affects its applicability. The solution to this problem seemed elusive, until in 1998, a group of researchers found that light could be transmitted through a metal surface with a pattern of holes on it, each with a diameter one-tenth of the light used. which should have been impossible because of the diffraction limit [2]. It was later seen that this transmission of energy on the metal surface was due to the generation of collective oscillations of free electrons present in the metal, which are known as surface plasmons. This is one of the major ways in which electromagnetic waves and electrons in a metal interact, and the branch of science that studies these phenomena is known as plasmonics. Plasmonics allows us to utilize light for communication via nanoscale devices, combining the best of electronics and photonics, which is why this relatively new field has been growing in importance over the last couple of decades.

Accelerated motion of charges creates electromagnetic waves, and the same is the case with surface plasmons. Electron oscillations in surface plasmons generate electromagnetic fields near the metal surface, both into and out of the metal, and the surface plasmon coupled with its companion em field is called a surface plasmon polariton (SPP) [3]. Surface plasmon polaritons are what takes the place of electrons and photons as information carriers in plasmonic devices. These are formed at the interface of two materials across which the real part of permittivity changes its sign. ie, of the two materials, one must be a dielectric (positive real permittivity) and the other a conductor (with negative real permittivity) [4].

The high reflectivity of metals to visible light is attributed to the collective oscillations of the free electrons of the metal under the influence of the incident wave, and then re-emitting those waves with the same frequency. However, when the em wave oscillates too fast for the electrons to follow (because of their inertia), the metal loses its reflectivity, and the em wave gets transmitted through the metal. The boundary dictating these two phenomena is called plasma frequency, and is a quantity that depends only on the number density of electrons in the metal [5]. The

plasma frequency is perhaps the most important plasmonic property of a metal, for it tells us for what frequencies the metal can act as a plasmonic device. Metals can support surface plasmon generation only for frequencies that are lower than its plasma frequency. In addition, ohmic losses in the metal are minimal for SPPs with frequencies close to the plasma frequency of the metal, which means the SPP will be able to cover more distance over the metallic surface [3]. Thus for a given em wave of a particular frequency, plasma frequency is the primary property by which we decide which metal to use for plasmonic applications.

The formula for the plasma frequency of a material can be derived in the following way. Here, the term plasma is used in a general way, to denote any material where only the electrons move and the ions remain stationary. Consider a block of plasma where the electrons have shifted by a distance x, and the ions have remained stationary. Now, the charge built up per unit area

$$\sigma = Nex$$

where N is the number density of electrons in the material and e is the magnitude of charge of an electron. The electric field in such a situation is given by

$$E = \frac{\sigma}{\epsilon_0}$$

$$E = \frac{Nex}{\epsilon_0}$$

The equation of motion of an electron in the material is thus

$$m^* \frac{d^2x}{dt^2} = -eE$$

where m^* is the effective mass of an electron in the plasma. The equation reduces to

$$m^* \frac{d^2x}{dt^2} = -e\frac{Nex}{\epsilon_0}$$

$$\frac{d^2x}{dt^2} + \frac{Ne^2}{\epsilon_0 m^*}x = 0$$

This is the equation of a simple harmonic oscillator with frequency

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}}$$

ω_p is the plasma frequency of the material, and as is clear from the equation, depends only on the number density of electrons in the material [6].

The present work focuses on finding the plasma frequency of two metals - copper and aluminum, by preparing thin films and measuring free electron density. Copper and aluminum were selected because they are metals whose plasmonic properties have already been extensively studied, and could serve as a measuring scale for the accuracy of the current work. Metal thin films were prepared by dc magnetron sputtering, and multiple samples of each metal were produced under different sputtering conditions. Material formation was analyzed by X-ray diffraction, and their surface morphology was checked to ensure film uniformity by scanning electron microscopy. Finally, hall measurement was used to find free electron concentration, from which the plasma frequency of the metals were calculated. The calculated plasma frequency values are then compared to reported values in literature.

2 Sample Preparation and Characterization

2.1 DC Magnetron Sputtering

Thin films of the metals were deposited onto glass substrates using a dc magnetron sputtering machine. Sputtering is a physical thin film deposition process in which particles are ejected from the target material and onto the substrate due to bombardment of the target by high energy particles [7]. It is one that is now commonly used to prepare thin films of high quality. The material whose surface is to be coated (called the substrate) and the source material (called the target) are kept inside a vacuum chamber into which an inert gas is pumped. An electric field is then used to create a gaseous plasma and accelerate the ions onto the target material. On collision, the gaseous ions transfer their energy to the target molecules or atoms, which get dislodged from its surface. These target molecules then collide with the substrate and stick there, forming a thin film. In magnetron sputtering, magnets are placed beneath and around the target (which is the cathode), which create a local magnetic field above the target. The electrons in the plasma get bound in this magnetic field, and this causes an extensive increase in plasma formation just above the target surface. This leads to an increase in ions striking the target, and thus to an increase in sputtering yield [8].

A dc magnetron sputtering device was used for this study, with argon gas. The factors that control film thickness are the working pressure, the dc power, the time of sputtering, the rotation speed of the substrate, the flow rate of argon and the distance between the target and the substrate. These values had to be optimized to make films that could be used to study the plasma frequency.

For the present study, the machine used was BC-300 DC Vacuum Sputtering Unit by Hind High Vacuum Ltd.The distance between the target and the substrate was kept fixed at 10cm and the substrate rotation speed at 17 rotations per minute for all samples. The remaining parameters were tweaked over successive coatings with the object of obtaining a smooth film that is completely opaque. The thin film samples that were thus obtained are given in table 1. Based on the results, the samples that were used for further study are A4 and C1.

2.2 X-Ray Diffraction Analysis

After the thin films have been coated, it is necessary to make sure that the film has indeed been coated by the target metal we used, and has not been contaminated by other materials that may have been inside the vacuum chamber. It is also necessary to check whether the film has been oxidized, in which case it won't be able to conduct electricity, and thus won't show plasmonic behavior. This is done by the help of X-ray diffraction analysis. When an X-ray beam is directed at a material, they get diffracted by the atoms present in the material. If the material particles have any kind of order, ie if the material shows some amount of crystallinity, the

Table 1: Thin films coated and their sputtering conditions

Sample code	Metal	Working Pressure (mbar)	Voltage (V)	Current (A)	Argon Flow Rate (sccm)	Sputtering Time (min)	Visual Observation
A1	Aluminum	$1.6*10^{-2}$	400	0.30	25.7	5	Semi-transparent
A2	Aluminum	$1.6*10^{-2}$	400-690	0.30	25.7	10	Semi-transparent
A3	Aluminum	$1.6*10^{-2}$	400-700	0.40	25.5	7.5	Semi-transparent
A4	Aluminum	$1.6*10^{-2}$	400-900	0.40	25.5	10	Opaque
C1	Copper	$6.2*10^{-3}$	434-496	0.30-0.60	28.4	5	Opaque

diffracted X-rays will have high intensities in some directions because of constructive interference, and different high intensity diffracted beams can be obtained as the incident angle of the X-ray beam is changed [9]. Plotting the intensity of diffracted rays against the angle at which they were obtained, the diffraction pattern of a sample is determined. The diffraction pattern will be the same for samples that are made of the same material and have the same crystal structure, allowing us to identify and compare different samples.

The angles at which intensity peaks are observed, or constructive interference takes place, is given by Bragg's equation, which is

$$2d \sin\theta = n\lambda$$

where d is the spacing between the planes, θ is the incident angle of the X-ray (as given in the figure 1), n is any integer and λ is the wavelength of the X-ray used. The reason that X-rays are used for this purpose is because the spacing between planes in crystals are typically of the same order of X-ray wavelength, thereby giving excellent resolution [10].

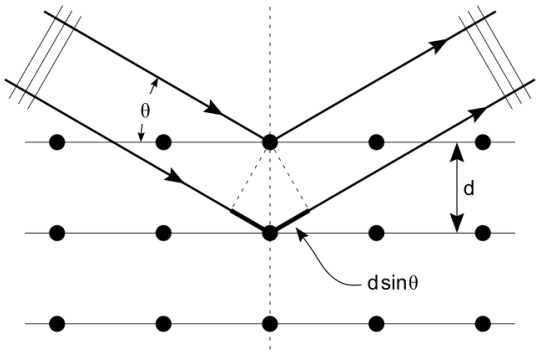


Figure 1: X-ray diffraction from different planes.

In the present study, X-ray diffraction analysis was carried out immediately after the films were coated to certify that the metals were properly coated, and no oxidation had taken place before hall measurement. The setup used was Rigaku Ultima IV X-Ray Diffractometer. The X-ray diffraction image of the copper C1 sample is given in figure 2, and the ICDD pattern used for comparison is 01-071-4610.

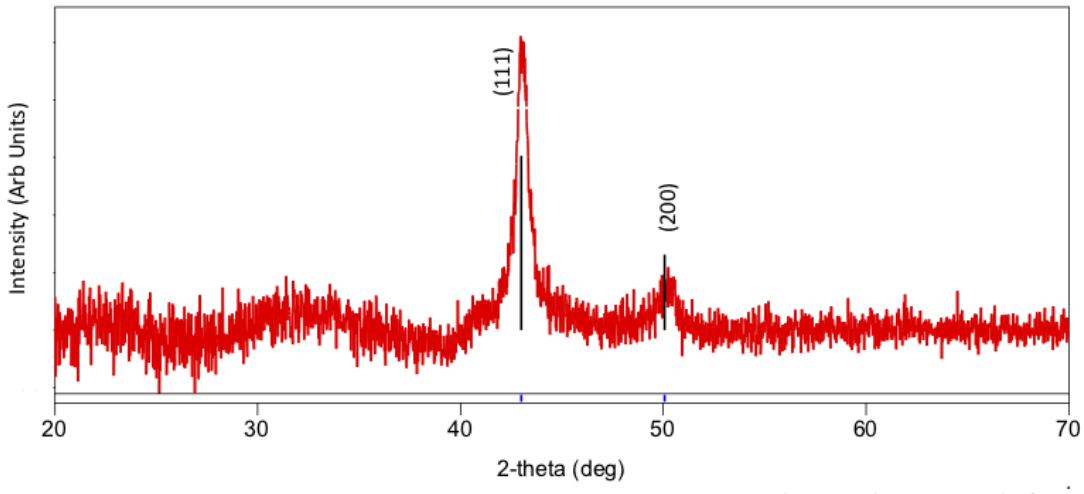


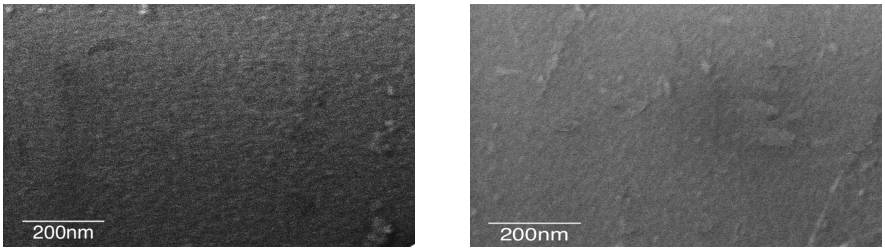
Figure 2: X-ray diffraction pattern of C1 sample.

2.3 Scanning Electron Microscopy

In simple terms, scanning electron microscope is a microscope that uses an electron beam instead of light to take images of objects. Light can only be used to view objects whose size is of the same order as its wavelength, which is why normal light can't be used to view objects in the nanoscale. In an electron microscope, an electron beam is used to illuminate the sample, which has a much smaller wavelength than that of visible light. The electrons reflect off the material and interfere with one another, and this information is collected via detectors. From this, an image of the sample surface is constructed, one which has much higher resolution than that that could be achieved by light.

When the electron beam strikes the sample surface, two types of electrons emerge back from it - secondary electrons and backscattered electrons. When the electron beam collides with the atoms on the surface, the atoms move to an excited state by gaining energy from the collision. They then emit electrons, which are known as secondary electrons. The surface characteristics or topography of the material is the primary factor that determines the number of secondary electrons ejected. Backscattered electrons, on the other hand, are constituents of the electron beam that are scattered on elastic collision with the atoms in the material [11]. The number of backscattered electrons increases as the atomic number increases. Hence these can be used to distinguish different materials in the same sample.

Zeiss Evo 18 Research scanning electron microscope was used in this study. The surfaces of the two samples A4 and C1 were observed under SEM and the images are given in figure 2. As is clear from the images, the surfaces exhibit a smooth and continuous coating, which attests to the uniformity of the film. There are no visible cracks or discontinuities, which will increase the accuracy of hall measurements subsequently taken.



(a) A4 (b) C1

Figure 3: SEM images of samples

Table 2: Hall analysis data

Sample Code	Free Electron Concentration cm^{-3}
A4	$2.780 * 10^{23}$
C1	$6.803 * 10^{22}$

2.4 Hall Analysis

The hall effect is the production of a voltage perpendicular to the flow of current in a conductor in the presence of a magnetic field that is itself perpendicular to the current. The voltage so produced is called the hall voltage. The hall voltage is inversely proportional to the number of free charge carriers in the sample material, and the magnetic field, current through the wire and thickness of the film known, it is possible to calculate the charge carrier concentration by the equation

$$N = \frac{IB}{V_H te}$$

where V_H is the hall voltage, t is the sample thickness, e is the electron charge, and I and B are the current and magnetic field respectively [12].

Hall measurement was carried out using Ecopia HMS-3000 system with a magnetic flux density input system of 0.54T. Hall analysis was done for the two samples A4 and C1, and the results obtained are given in table 2.

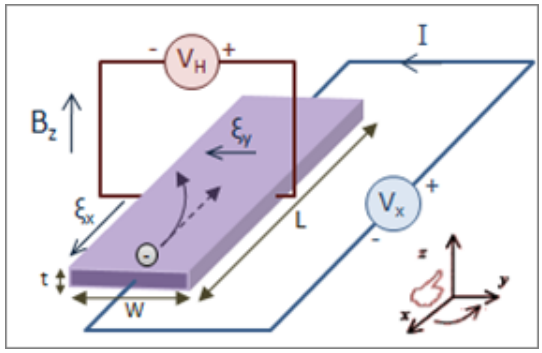


Figure 4: Hall measurement schematic diagram.

2.5 Calculations

From the free electron concentration obtained by hall analysis, the plasma frequency of the two metals are calculated by the equation

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}}$$

where $e = 1.6 * 10^{-19}$, $\epsilon_0 = 8.854 * 10^{-12}$, m^* for the metals have been taken from literature [12], and N has been obtained. The plasma frequency obtained through this equation is the angular frequency, which was divided by 2π to get the actual frequency. The calculated plasma frequencies are reported in table 3 in units of nanometers (nm) and electron volts (eV).

Table 3: Calculated Plasma Frequencies

Sample Code	Free Electron Concentration (m^{-3})	Effective Electron Mass (kg)	Plasma Frequency (nm)	(eV)
A4	$2.780 * 10^{29}$	$1.24 * 10^{-30}$	75	16.52
C1	$6.803 * 10^{28}$	$1.18 * 10^{-30}$	146	8.49

3 Results

Metal thin films of aluminum, copper and titanium were prepared by dc magnetron sputtering, and their composition and surface characteristics were checked by X-ray diffraction and scanning electron microscopy analysis respectively. The free electron concentrations of these metals were obtained by hall measurement, which was then used to calculate the plasma frequency of the metals. A comparison of the values obtained by the present study and those reported in literature is given in table 4. The obtained plasma frequency of aluminum and copper fall in the range of values present in literature.

Table 4: Plasma frequency value comparison

Metal	From present study (eV)	From previous studies (eV)
Aluminum	16.52	15.3 [13] 14.75 [14] 12.04 [15] 15 [16]
Copper	8.49	7.39 [14] 8.76 [15]

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