STUDY OF ELECTRICAL AND OPTICAL BEHAVIOR OF METAL AND METAL OXIDE NANOSTRUCTURES

Abstract

Preparation of ZnO and copper nanoparticles was done using sol-gel technique. Sol-gel technique helped us to get solutions which was further drop coated on glass substrates. The film so obtained was characterized using X-ray diffraction (XRD), UV-Vis spectrophotometer and electrical conductivities were measured using two probe method.

The results obtained from spectroscopy measurements were analyzed to obtain band gap of ZnO. Copper, on the other hand showed surface 163lasmon resonance. Also, the electrical conductivities were measured using digital multimeter. It was seen that copper film showed a conducting nature whereas ZnO film was non conducting at room temperature.

Keywords: Sol-gel, BandGap, Copper, ZnO, Nanoparticle.

Authors

Parul Yadav
Departmentof Physics
Maitreyi College, Chankayapuri
University of Delhi
pyadav@maitreyi.du.ac.in

Mansi Dhingra
Departmentof Physics
Maitreyi College, Chankayapuri
University of Delhi
mdhingra@maitreyi.du.ac.in

I. INTRODUCTION

Electrical and optical properties of metal and semiconductors have long been studied. But when we take any material to nanoscale it shows a new range of properties which can be understood by various characterization techniques. Metal which is supposed to be highly conducting in macroscopic dimension when reduced to microscopic dimension shows an altogether different property. Similar is the case with semiconductor nanofilms [1-3]. It is believed that on approaching nanoscale lengths the continuous structure of energy bands get converted to discrete energy levels.

It is important to understand the basic differences between metal and metal oxide nanoparticles. The following table gives some of the basic differences:

Aspect	Metal Nanoparticles	Metal Oxide Nanoparticles
Definition	Consist of pure metal atoms	Consist of metal atoms bonded to oxygen atoms
Chemical Composition	Elemental metal	Metal + Oxygen
Properties	Metallic properties	Combination of metallic and oxide properties
Reactivity	Generally more reactive	Often less reactive due to oxide layer
Stability	Prone to oxidation and corrosion	More stable due to oxide layer
Color	Typically have metallic luster (shows SPR)	Often have distinct colors (Absorbs energy corresponding to band-gap)
Electrical Conductivity	High electrical conductivity	May have reduced conductivity
Applications	Catalysis, electronics, etc.	Catalysis, sensors, ceramics, etc.

Metals like copper, aluminum, and titanium exhibit Plasmon resonances in UV-visible-near infrared regions, making them popular as a replacement for aluminum in integrated circuits and printed circuit boards. Copper's superior electrical conductivity and heat dissipation capacity make it preferred in heat sinks and heat exchangers. Surface plasmons (SPR) are collective oscillations caused by light interaction with free electrons in metal nanoparticles, including gold and silver. Faraday's 1850s study on the optical properties of metal nanoparticles in colloidal solutions led to the first significant scientific study of these properties [4]. Gustav Mie's 1908 work on extinction properties of metal spheres further contributed to the understanding of SPR [5].

ZnO, a highly stable semiconductor with a band gap of 3.3 eV, is a promising candidate for various device applications, including photovoltaic devices and gas sensors. As a member of the II-VI family, it is n-type and widely used in various applications [9].

Metal which have its conduction band and valence band overlapping in macroscopic length scales tend to show an energy bandgap (difference between conduction and valence band energies) at nanometer scale. Also reflected in its optical properties where it absorbs that particular light from the electromagnetic spectrum which give rise to collective oscillations commonly known as surface plasmons.

On the other hand the semiconductors which are believed to have a band gap at macroscopic scales are expected to show an increase in the values of energy band gap at microscopic scales.

In this chapter, we have synthesized Copper nanoparticles (metal) solution reduction process and ZnO nanoparticles (semiconductor) using sol gel technique. In order to compare the optical properties of the two, measurements were carried out using UV-Vis spectrophotometer whereas the electrical measurements were carried out using Digital multimeter.

II. EXPERIMENTAL DETAILS

1. **Synthesis of Metal Oxide and Metal Nanopowders:** Synthesis of nanostructures of uniform shape and size is extremely important in accordance with the extensive development of nanotechnology for their potential applications. A large number of synthesis methods are used to achieve this goal. The wet chemical route for the synthesis of nanostructures has been done and optical as well as electrical studies are carried out under this project.

   To synthesize the ZnO nanoparticle, we have chosen bottom up approach as we started our synthesis from molecular level using the chemical reactions .Firstly, known weights of zinc acetate were mixed in ethanol according to their molar ratios .To prepare ZnO nanoparticles, approximate amounts (for 0.3M solution, 6.5814 g was added in 100 ml of ethanol) of zinc acetate were mixed in ethanol according to the formula:

$$Zn(CH_3COO)_2 + 2\,CH_3CH_2OH \longrightarrow 2\,Zn(OH)_2 + CH_3CH_2CH_2COO \xrightarrow{\text{(at } 300^0\,\Delta C)} ZnO + H_2O + CH_3CH_2CH_2COO$$

   The synthesis of copper nanopartcles involved using analytical grade reagents without further purification. The nanoparticles were synthesized through a solution reduction process using sodium borohydride as a reducing agent.

   The blue copper ammonia complex was formed by adding 1 g copper metal to a 27% ammonia solution. Dilute HCl (5%) was added to the blue solution, and 100 ml of 0.25 M NaBH4 solution with 4 g starch was added. The solution turned dark brown, confirming the formation of the Cu nanomaterial. The prepared nanomaterial was separated by centrifugation at 4000 rpm.

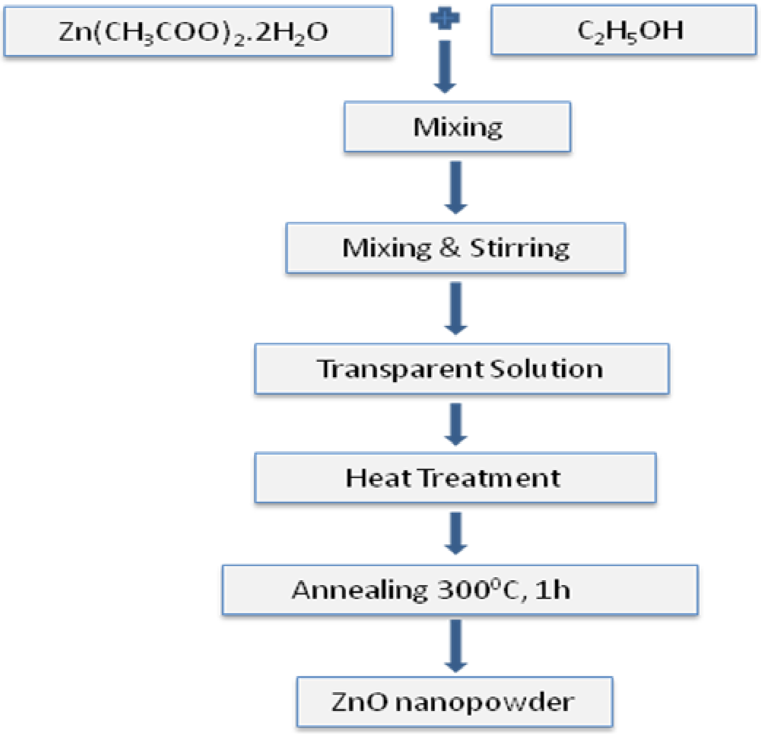

Figure 1: Schematic of Preparation ZnO Nanoparticles

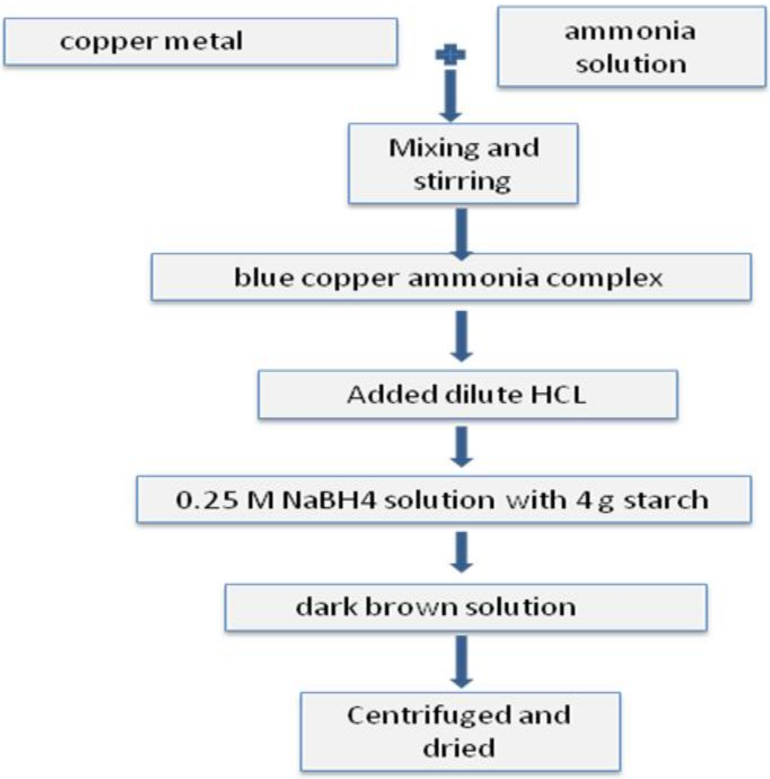

Figure 2: Schematic of Preparation Copper Nanoparticles

III. RESULT AND DISCUSSION

1. **Structural Studies:** The nanopowders' structural characterizations were studied using X-ray diffraction (XRD) at room temperature using a Philips XPERT-PRO diffractometer system (2 theta range was taken from 40 º to 80 º) and Cu Kα radiation at 1.5406 Å wavelength.

Figure 1 shows the XRD patterns of different copper nanopowder. The XRD patterns were indexed using standard database (JCPDS). For prepared sample, lattice parameters were calculated for FACE CENTERED CUBIC structure for copper and HEXAGONAL structure for ZnO. The average crystallite size of the copper nanoparticles was estimated using the Scherrer formula which is given as:

$$D_{hkl} = \frac{k \times \lambda}{\beta_{hkl} \times \cos\theta_{hkl}}$$

where D_{hkl} represents the particle size perpendicular to the normal line of (h k l) plane, k is a constant (0.9), β_{hkl} represents full width at half maximum (FWHM) of the (h k l) diffraction peak, Θ_{hkl} represents the Bragg angle of (h k l) peak and λ is the wavelength of X-ray. It shows that the average crystallite sizes are around 7 nm and lattice parameter was found to be 2.77 Ǻ for copper nanoparticles.

For ZnO, average crystallite size was found to be approx 50 nm and lattice parameters a= 3.41Ǻ and c= 5.28 Ǻ.

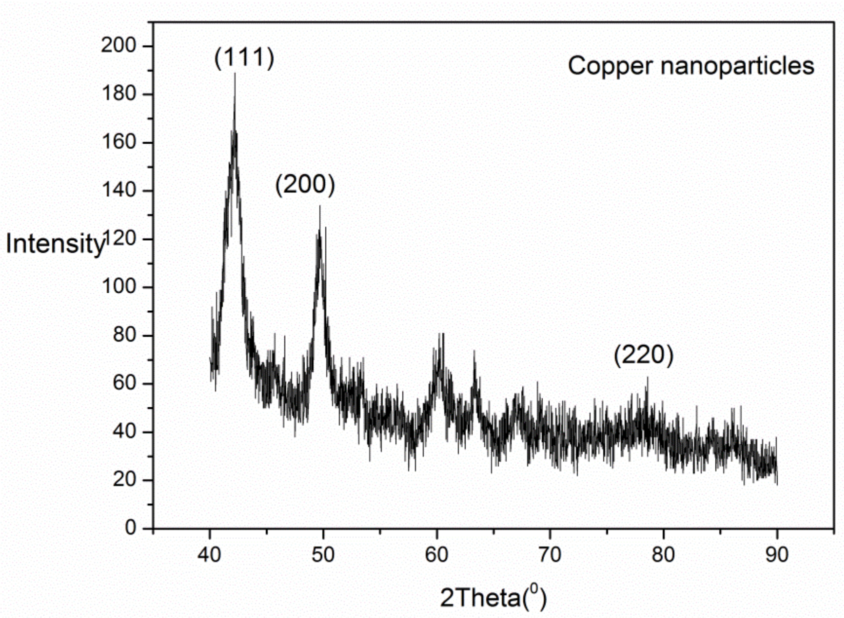

Figure 3: XRD Pattern of Copper Nanoparticles

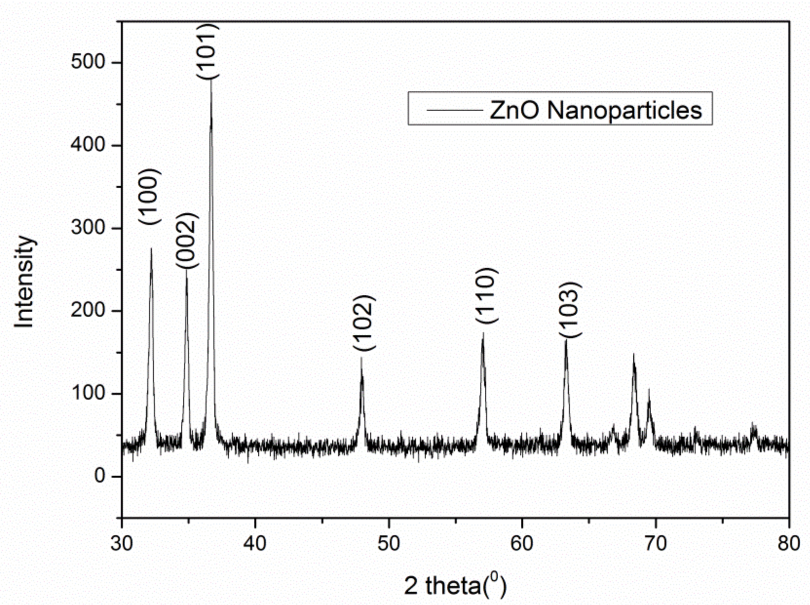

Figure4: XRD Pattern of ZnO Nanoparticles

2. **Optical Study:** Absorbance spectra were recorded at room temperature for the wavelength range 300-800 nm for prepared samples. We recorded the absorbance spectra of the samples of ZnO and copper nanoparticles by UV- visible spectroscopy and plotted them in the graph as shown in figure 5. Absorbance peak of ZnO is found to be 369nm. .So from the above data we can see that the ZnO nanoparticles absorb UV radiation as the energy band gap (3.3eV) of ZnO corresponds to UV wavelength region. [Since E (in eV)=1234/wavelength(in nm) = {1234/369} eV = 3.34 eV~3.3eV]. For copper (Cu) nanoparticles, absorbance peak is centered at 542 nm which lies in visible region so this peak is due to surface Plasmon resonance (resonance of electron oscillation with light).

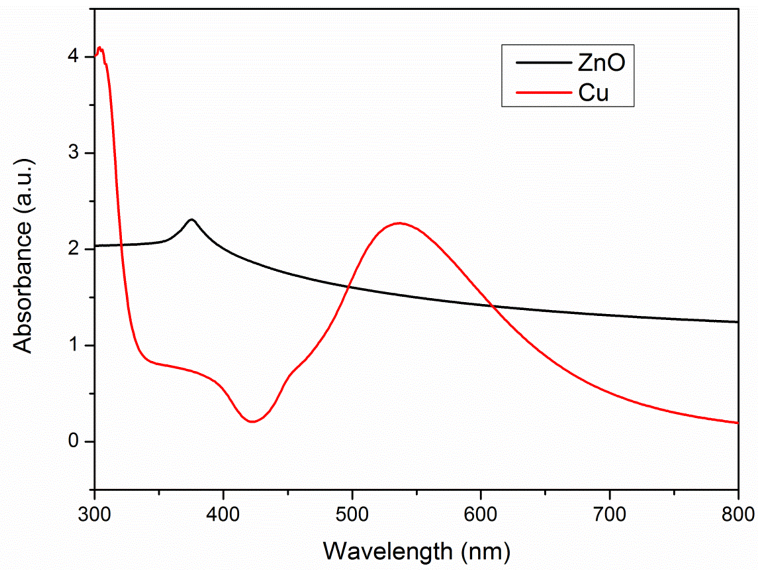

Figure 5: Absorption Spectra of ZnO and Cu Nanoparticles

3. Electrical Study

- **Direct Current (Dc) Conductivity Measurement:** There are two methods to measure DC electrical conductivity: Two probe measurement, and four probe measurement. As the names suggest, two probe measurement measures electrical conductivity by simultaneously contacting a sample in two places, while four probe measurement measures conductivity by simultaneously contacting the sample at four places. The Two Probe Method is a widely used method for measuring resistivity in high-resistivity samples like polymer sheets/films, surpassing the FourProbe Method's range.

  Two Probe DC conductivity measurements involve constant current flow through a sample, determining potential difference, and determining resistance using Ohm's law. The conductivity of the sample is determined using sample dimensions and resistance.

  In Figure 6, a schematic is shown of the two probe measurement technique to obtain conductivity of the sample. The copper and ZnO nanoparticles were coated on non-conducting substrates to form a continuous film. Here we measured the resistance of the copper film which is found to be 0.22 kohm. Resistance of ZnO film has also been measured which behaves like open circuit at room temperature.

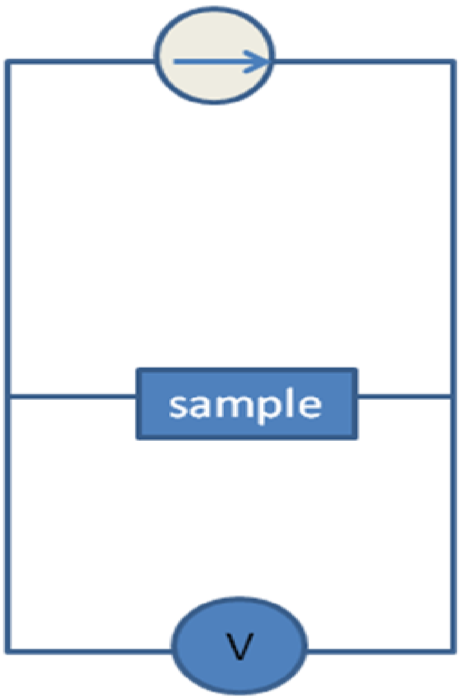

Figure 6: Schematic of Two Probe Method to Measure Electrical Conductivity

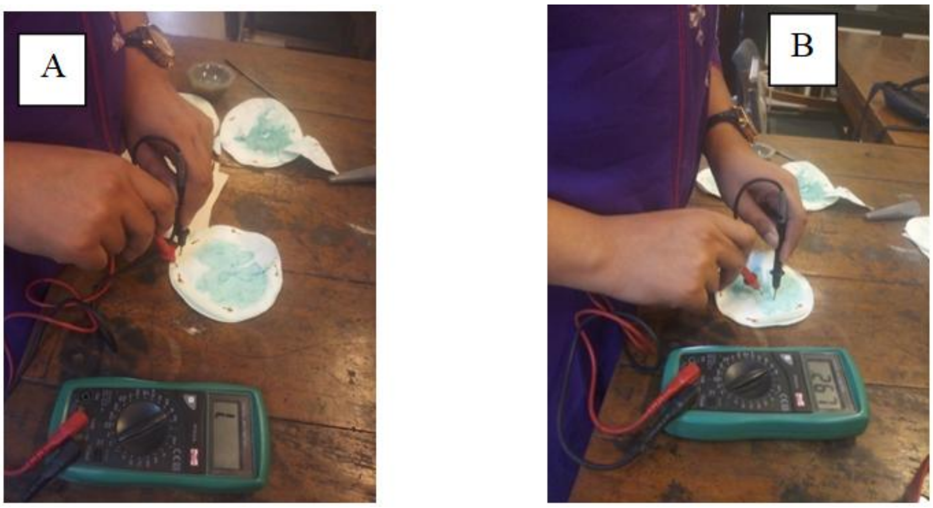

Figure 7: Electrical Conduction Seen Using Digital Multimeter for Two Cases (A) When There Is No Film) (B) At The Surface Of The Copper Film

IV. CONCLUSION

In this project we prepared metal (copper) and semiconductor nanoparticles using chemical method and their structural and optical properties have been investigated. Structural properties of both nanoparticles were studied using XRD patterns. XRD confirms the synthesis of nanopartcles. In optical study, we found that absorbance peak in ZnO nanoparicles is because of its optical bandgap whereas in copper nanopartcles, it is due to surface plasmon resonance. The electrical measurements also justified the unique nature of metal and metal oxide nanostructures.

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REFERENCES

[1] C.P. Poole, Jr. Frank J. Owens, Introduction to Nanotechnology (Wiley India Pvt.Ltd.).
[2] S.K. Kulkarni, Nanotechnology: Principles & Practices (Capital Publishing Company)
[3] K.K. Chattopadhyay and A. N. Banerjee, Introduction to Nanoscience and Technology (PHI Learning Private Limited).
[4] M. Faraday, Philos. Trans. 147, 145 (1857).
[5] G. Mie, Ann. Physik IV 25, 377-445 (1908).
[6] Bohren, C. F.; Huffman, D. R. Absorption and Scattering of Light by Small
[7] Particles; John Wiley & Sons: New York, 1983.
[8] M. Vafaee, M. S. Ghamsari, Preparation and characterization of ZnO nanoparticles by a novel sol...gel route, Materials Letters, 61 (2007) 3265
[9] Hosono, S.Fujihara,T. Kimura, H.Imai, Growth of layered basic zinc acetate in methanolic solutions and its pyrolytic transformation into porous zinc oxide films, Journal of Colloid and Interface Science, 272 (2004) 391
[10] M. Dhingra, L. Kumar, S. Shrivastava, P. S. Kumar, S. Annapoorni Bull. Mater. Sci., Vol. 36, No. 4, August 2013, pp. 647–652. Indian Academy of Sciences.

