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Electrical Conductivity and Band Gap Energy Study of Some Transparent Conducting Metal Oxide and Sulphide Nano Materials

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Abstract : Nano structured metal oxide and sulphide materials are having a fairly high conductivity due to the presence of high carrier concentration in the crystal lattice and also due to the surface to volume ratios. The nano structured oxides are most useful in the development of optoelectronic devices. Several investigations have been carried out on the transparent conducting oxide nano materials mainly because of their variety of applications. It is known that these TCO materials the transparency (in the visible region) is a result of the wide band gap of the material and the n type conductivity is mainly due to the oxygen ion vacancies that contribute to the excess of electrons on the metal atoms. Due to the above importance, we prepared the nano structured CuO, ZnO, and CdS materials using microwave assisted solvo thermal reactions and chemical precipitation method. The above synthesized nano materials were investigated by temperature dependent electrical resistance, capacitance, dielectric constant (ϵ_r) and electrical conductivity (σ) measurements. The electrical conductivity measurements over a temperature range 343K - 423K reveal that the temperature dependence of electrical conductivity increases with increasing temperature and particles size decreases. The study reveals that CuO, ZnO, ZnS and CdS nano particles have negative temperature coefficient of resistance. Band gap energies studies confirm this particle size reduction leads to reduce the energy gap. Results were discussed in details.

Introduction

Metal oxides and sulphides that exhibit a high optical transmittance and in addition are highly electrically conductive are referred to as transparent conductive oxides (TCO's)¹. They can also be described as wide band gap oxide semiconductors. Examples of compounds with in this material class CuO,ZnO,CdS. Since the band gaps of

these materials lie in the ultraviolet wavelength region they do not absorb visible light as a consequence, they appear transparent to the human eye. If such an oxide and sulphide is doped with a sufficient amount of suitable ions, high electrical conductivities can be achieved. TCO's are of major technical importance since thin films exhibiting a high electrical conductivity and optical transmittance are needed in for instance, solar cells, flat panel displays and electrochromic devices²⁻³. TCO films are commonly produced via vacuum based gas phase methods, such as magnetron sputtering or chemical vapor deposition⁴⁻⁵. Due to the high crystalline and compactness of the resulting thin films, excellent conductivities can be achieved. There has been increasing interest in the synthesis and study of inorganic nanostructures in recent years for their widely varying properties and potential applications.⁶⁻⁹ Metal oxide nanostructures with well controllable size and shape have received increasing attention in current material synthesis and device fabrication¹⁰⁻¹².

In recent years, considerable interest has been focused on metal oxide nano particles that are extensively used in a number of applications due to their possession of enthralling electrical, optically catalytic and magnetic properties¹³⁻¹⁷. Among metal oxides, copper oxide and zinc oxide nano particles have been of great interest due to their potential applications in many important fields of science and technology such as gas sensors, solar-cells, field emitters, piezo-electric nano generators, light emitting diodes (LED), excellent photo catalyst and nanooptoelectronic devices.

Preparation of CuO Nano Particles.

Copper oxide nano materials were synthesized by 6.9 g of copper II sulphate pentahydrate is mixed 50ml of distilled water and Fehling solution of 6ml and sodium hydroxide 12g with 50ml of distilled water. Then these two solutions are mixed and added 2ml triton x-100 and 5g of glucose. Then the solution is completely mixed by vigorous stirring by a magnetic stirrer at 60°C for 2 hours. Red precipitate is obtained. The product was filtered and dried at room temperature for removing moisture and the collected specimen were annealed gradually increases at 0°C to 100°C. Thus the copper dioxide nano material was synthesized by different concentration with different temperature.

Preparation of ZnO Nano Particles.

Zinc oxide nano materials are synthesized by 7.6g of zinc acetate and 1ml of triethanolamine and 3g of NaOH with 50ml of distilled water. Then the solution is completely mixed by vigorous stirring at 60°C for 1 hour and 30 minutes till a white precipitate is obtained. The product was filtered and dried at room temperature for removing moisture and the collected white precipitate is annealed gradually from 0°C to 100°C. Thus zinc oxide nano materials is synthesized for different concentration with different temperature.

Preparation of CdS Nano Particles.

CdS nano particles have been synthesized through chemical precipitation technique. Aqueous solution of cadmium acetate [(CH₃COO)₂ Cd 2H₂O] 1 mole with 100 ml of distilled water was stirred with 700 – 1000 rpm for 1 h at room temperature. Aqueous solution of sodium sulfide (Na₂S) 1 mole with 100 ml of distilled water was added drop wise to cadmium acetate solution and was stirred with 700 - 1000 rpm for 2 h. A precipitate with yellowish orange colour was formed soon after the addition of the Na₂S. The colour of the solution appeared to be yellowish orange indicates the formation of cadmium sulfide. In order to decrease the grain size increase the stirred time. The nano particles were initially purified by precipitating the particle with excess double distilled water to remove the impurities. The washed particles were centrifuged at 2000 rpm for 10 min. Finally wet precipitate was dried in microwave oven at 50°C for 10 minutes. CdS nano particles were obtained as precipitate after being dried at room temperature.

Electrical Conductivity Measurements of CuO,ZnO,CdS nano particles

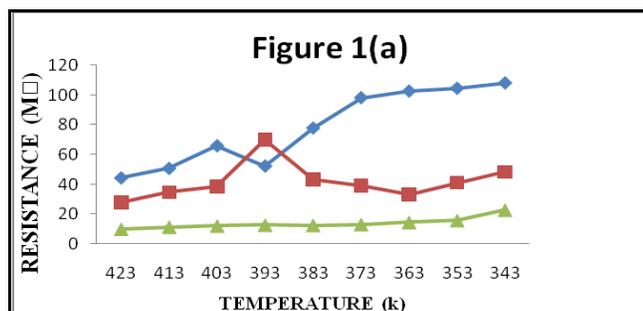
The two probe method was used to study the electron transport properties of as prepared CuO, ZnO and CdS nano particles. A self-made two probe apparatus was used to study the electrical properties. The apparatus was consisting of two electrodes with a heater in a cylindrical aluminum body for measuring temperature dependent electrical conductivity. The contact to CuO, ZnO and CdS nano particles was made a pallet using a palletizer conducting silver paste on an area approximately 0.8mm x 0.5mm. The CuO,ZnO and CdS nano particles were therefore sandwiched between the two metal plates. The temperature dependent electrical conductivity was measured by increasing the temperature surrounding the nano particles in the temperature range 343- 423K. The applied dc voltage kept constant across the nano particles during temperature dependent electrical measurements.

1. Temperature Dependent Electrical Resistance

The temperature dependence of electrical resistance was measured over a temperature range of 343K - 423K. All the studies were carried out in a self- made two electrode apparatus.

Variation of electrical resistance with temperature

The measured temperature dependence resistance over a temperature range of 423-343K of CuO,ZnO and CdS nano particles is shown in fig 1(a). The results reveal that the resistance (RT) of nano particles of all diameter rises as the temperature decreases. The increase of resistance in the nano particles at low temperature attributes to the reduction of free carriers in the conduction band¹⁸, where only carriers with enough energy can stay in the conduction band for electrical conduction. The drop in carrier density at low temperatures suggests the overlapping of the conduction band and valence band where thermal energy is the main factor to determine the free carrier density. Therefore, the temperature dependent resistance measurement shows that the electrical conductivity of the CuO,ZnO and CdS nano particles is carrier density dependent. The exponential decrease in carrier density in low temperature range suggests that the CdS nano particles have semiconducting behavior. It is clear from figure 1(a) that the resistance (RT) of CuO,ZnO and CdS nano particles decreases with increasing temperature and exhibits an obvious negative temperature coefficient of resistance (TCR).



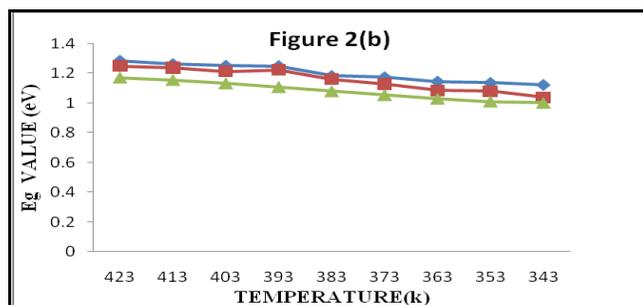
2. Band Gap Energy (Eg) Measurements

Band Gap Energy was calculated using the formula

$$E_g = 2K \left[\frac{2.303 \log_{10} RT}{1/T} \right]$$

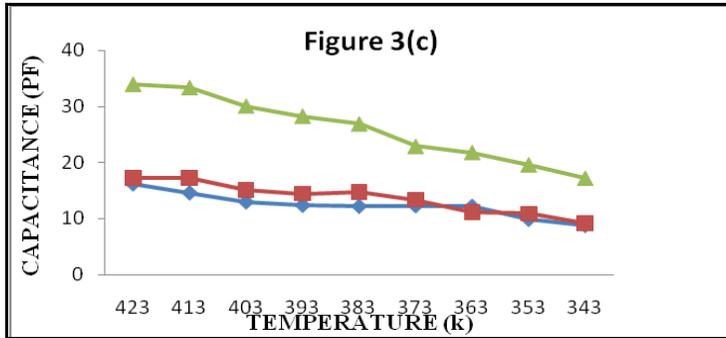
K is Boltzman constant ($K=1.38 \times 10^{-23}$), E_g is Band gap energy, T is temperature in Kelvin, R is resistance.

Variation of Band gap (Eg) with temperature



3 Temperature Dependent Capacitance

The temperature dependence of capacitance of CuO,ZnO and CdS nano particles of different concentration shown in fig 3(c). It is clear that the capacitance of CuO,ZnO and CdS nano particles increases with increasing temperature¹⁹.



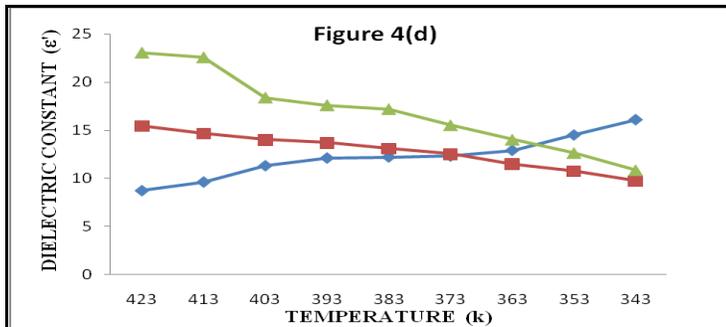
4. Dielectric Constant (ϵ_r) Measurement

Dielectric constant is calculated using the formula

$$\epsilon_r = Cd / \epsilon_0 A$$

C is capacitance in Farad, d is thickness of the CuO, ZnO and CdS pellet in mm, ϵ_0 is the Relative permittivity of vacuum and A is cross sectional area.

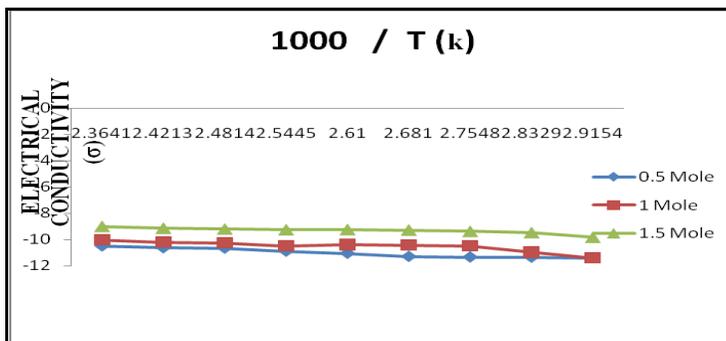
Variation of dielectric constant(ϵ_r) with temperature



5. Conductivity Measurement

It was observed that the conductivity increases with increase in temperature in all nano materials¹⁹ and this increase may be due to the increased electron-phonon interaction. Both the electron-electron and the electron-phonon interactions take part in the electron transport through the nano materials. As the temperature is increased, phonon induced effects dominates and electron-phonons interaction becomes more prominent. Further, such interaction dramatically enhances the electron transport in addition to phonon through nano materials due large carrier generation when temperature is increased.

Variation of electrical conductivity(σ) with temperature



Conclusion

The electrical conductivity study reveals that the electrical conduction in all the nano materials is temperature dependent and increases with temperature. The resistance of CuO,ZnO and CdS nano particles decreases with increasing temperature and thus have negative temperature coefficient of resistance (TCR).The conductivity measurements and band gap energy exhibit the above prepared CuO,ZnO and CdS material perfect behavior of nano particle.

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