STRUCTURAl , MICROSTRUCTURAL CHARACTERIZATION &
ELECTRICAL TRANSPORT STUDIES OF NANO CDS

V. S. Patil
Assistant Professor in Physics,Y. C. W. M. Warananagar, Tal-Panhala, Dist- Kolhapur.

C. B. Mane,
Assistant Professor in Chemistry,V. Y. M. Pethvadgaon. Tal-Hatkalagane, Dist- Kolhapur.

Manisha V. Patil.
Librarian, Shripatrao Chougule Arts & Commerce Mahavidyalaya, Malwadi-Kotoli. Tal- Panhala.Dist- Kolhapur.

Research Guide :
Madhav N. Rode
Vice- Principal,Vaidyanath college, Parali, Beed.

Abstract

The work mainly concerns with study of the structural details, microstructure, and optical properties of the CdS thin films. Various properties like optical absorbance, dc and ac conduction behavior have been investigated in close correlation with the microstructure of the films. It involves the study of nanocrystalline CdS thin films by sol-gel spin coating deposition techniques, studying growth, microstructure, and morphology and from that correlating the microstructure to its physical, electrical and optical properties.

Keywords *: morphology, microstructure*

Introduction

The study of semiconductor nanoparticles has been an interesting field of research for more than two decades. This is because it gives an opportunity to understand the physical properties in low dimensions and to explore their vast potential for applications, e.g. in optoelectronics [1-4]. The latter is particularly based on the large variations of the band gap as a function of particle size, which is a consequence of quantum confinement [5-11]. Moreover, small nanoparticles allow the study of relevant surface properties due to the high surface to bulk ratio. In semiconductor nanoparticles, strong confinement effects

appear when the size of the nanoparticles is comparable to the Bohr radius of the exciton in the bulk material. The confinement effect is observed for CdS particles when the particle sizes are equal to or less than 50 Å [9, 10]. Bulk CdS is widely used as a commercial photodetector in the visible spectrum. It is also used as a promising material for buffer layers in thin film solar cells [12, 13]. The optical properties of CdS nanoparticles have been extensively studied in recent years as this material exhibits pronounced quantum size effects [14, 15]. A lot of work has been done on the preparation of these nanoparticles, and a wet chemical synthesis has come up as a promising technique because of the ability to produce various sizes and large quantities of the nanoparticles [14, 16-18]. Since very small nanoparticles have larger surface to volume ratios, many properties are directly related to the particle surface. The surface properties of the nanoparticles have been studied much less than the bulk properties [19, 20], even though this information is of significant importance, and therefore many interesting aspects of nanoparticles are still not revealed. Photoelectron spectroscopy (PES) has a great potential to probe the surface of such particles. This is because of the small inelastic mean free paths of emitted photoelectrons,

Structure of CdS

Cadmium sulphide is a wide band gap semiconductor with Eg ≈ 2.5 eV [21]. It is used in photodetectors and for solar cell applications as n-type window layers in heterojunction devices [22]. The optical properties of CdS have been extensively studied [23, 24]. Quantum size effects are quite pronounced because CdS has a rather large rB (≈3 nm) [25]. CdS nanoparticles are attractive candidates for optoelectronic applications as it is possible to engineer the band gap over a wide spectral range (visible to UV).Bulk CdS has a hexagonal wurtzite-type (W) crystal structure with a = 0.4160 nm and c = 0.6756 nm [26]. Two other structures (see table 1) are observed *only* in nanocrystalline CdS [36]: (a) a cubic zinc blende (Z) phase under ambient conditions, and (b) a high-pressure rock salt phase [27]. The wurtzite to rock salt transformation involves not only a change in symmetry (hexagonal to cubic) but also a change in the nearest-neighbour atomic coordination (from four to six), whereas the wurtzite to zinc blende transformation involves only a change in symmetry. The two types of transition are affected by particle size in different ways.

There exists a large number of methods to obtain clusters with different properties. These were developed over many years. The cluster preparation methods can be classified in two general classes as gas phase methods and condensed phase methods. Often gas phase clusters are produced and studied in the gas phase only, or they are deposited on a solid surface. These methods are used for small quantities of clusters. The second class of synthesis is that in which the clusters are obtained in the condensed phase. These methods are mainly divided into two classes as chemical and physical methods. Chemical methods are promising in terms of cost reduction and ability to produce large amounts of particles. Usually the nanoparticles are being capped by different organic molecules since this is an easy way of stabilizing them to avoid agglomeration. CdS nanoparticles are of the great interest since many years. The reason may be that this small band gap material shows interesting size quantization effects (below the Bohr radius, i.e. 30 Å), and the nanoparticles can be obtained in macroscopic amounts for various characterizations, which is difficult for many other II-VI semiconductor particles excluding CdSe and to

some extend CdTe. An important aspect of research on nanoparticles has been to prepare size selected particles in order to study various size dependent features. There were many efforts to synthesize size selected CdS with a very narrow size distribution, however only a few were successful [2, 4,5]. Most of the techniques follow an organic capping route and a wet chemical synth

esis with solvents like ethanol, methanol, acetonitrile, dimethylformamide(DMF), etc. The particles are obtained as free standing powders and can be redissolved to form a "nanoparticles solution". Polyphosphate and thiols are the most commonly used capping agents. Use of monochromatic light to irradiate a colloidal solution of CdS particles was adopted in order to produce various sizes. Gel electrophoresis in order to separate sizes was used [23]. Monodispersed CdS particles can be found in the literature in a few cases [12], A report on photoemission studies also shows nice absorption spectra of two monodispersed CdS nanoparticles (produced in DMF) [15]. We have done an extensive literature search in order to reach our goal of producing highly monodispersed nanoparticles using wet chemical synthesis.

Materials and Methods
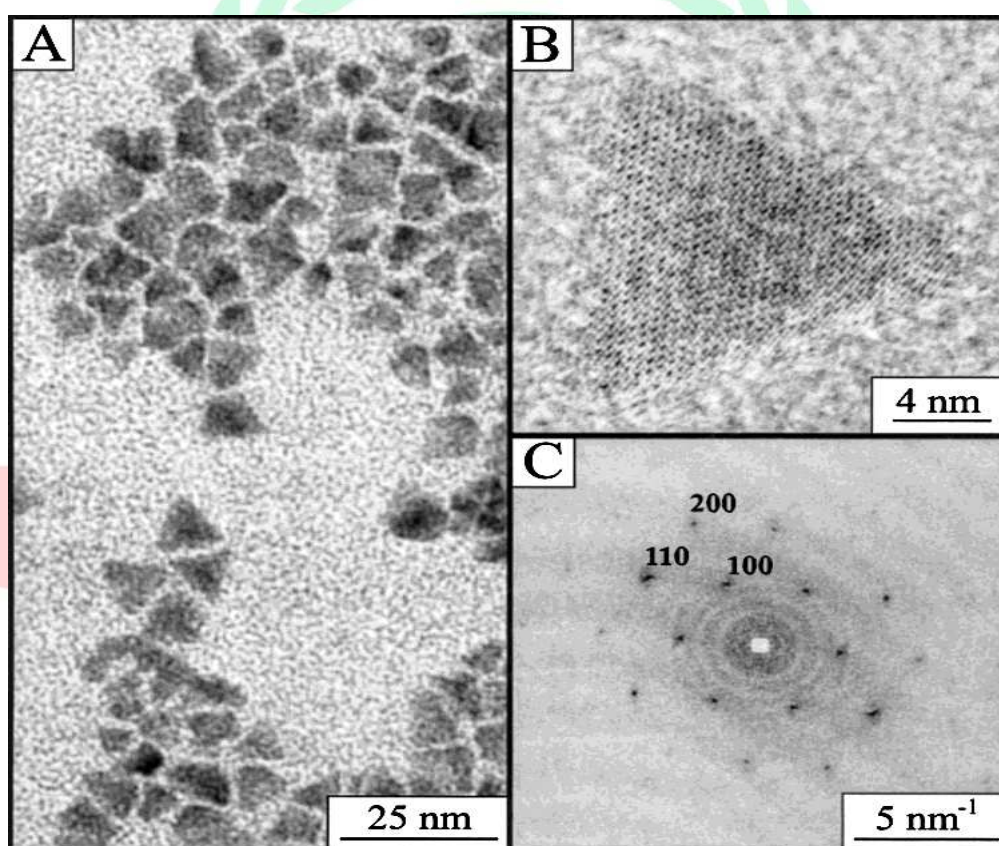
3.2.2 Transmission Electron Microscope (TEM)

Fig.1.A) TEM image of CdS triangular shaped nanocrystals. B) HRTEM of a nanocrystal. C) PS of this nanocrystals. The transmission electron microscopy (TEM) pattern (Fig. 1A) shows that most of the particles are characterized by an angular shape with an average size of 10 nm. To determine the structure of isolated triangular nanocrystals, high-resolution transmission electron microscopy (HRTEM) experiments and image processing by the square Fourier transform (power spectrum, PS) are performed. A large collection of triangular nanocrystals is used and the data

obtained are highly reproducible. The HRTEM image of the triangular nanocrystals shows several lattice planes (Fig. 1 B). The PS shows several well defined sharp spots: the inner three pairs are characterized by an inter-plane distance of $3.626A^0$. The second order is well defined. Another series of spots corresponds to a distance of $2.1094 A^0$ with a 60^0 angle between the spots. These experimental data are compared with the calculated single crystal diffraction patterns oriented in [111] and [001] direction for cubic (zinc blende) and hexagonal (wurtzite) structures, respectively. For the cubic phase, the first order external diffraction spots are observed. Conversely, for the hexagonal phase all the spots are present (inner and external).

Table 1 compares the calculated and experimental data of the inter-planar distances and shows rather good agreement between these data. The spots corresponding to 100, 110, and 200 diffraction of the hexagonal structure (wurtzite) are shown in Fig. 11C. Hence, from this, it can be concluded that isolated triangular nanocrystals are crystallized in a wurtzite structure. The well-defined second-order diffraction spots indicate a high crystallinity of the nanoparticles. The triangular shape of PS spots (Fourier transform form factor) indicates a highly homogeneous surface. Thus, at the few-nanometer scale it can be concluded that the isolated triangular particles are highly crystallized in a hexagonal structure with a homogeneous surface. Figure 2 also shows nanocrystals having other shapes. It is difficult to know if they result from coalescence after growth or they grow like that. However, from the results obtained with other nanocrystals the tendency will be to say that they grow like that.

Table 1. Calculated single crystal diffraction for the [001] plane of wurtzite CdS with electron radiation k = 0.02508A^{0} compared with the experimental results

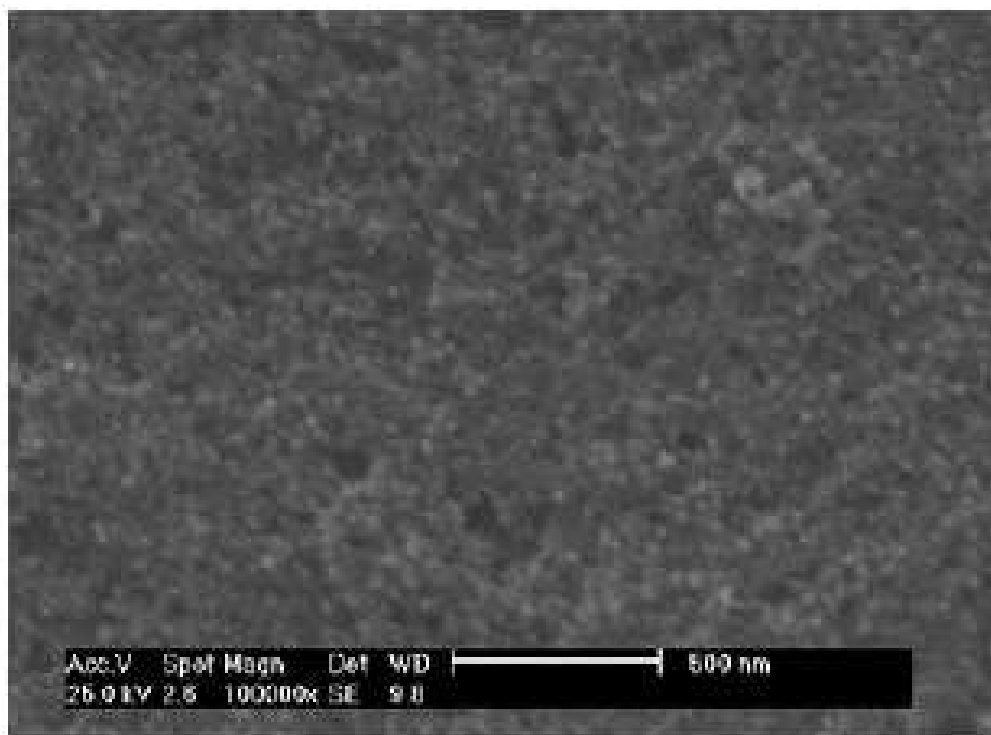| Diffraction	d calculated (A^{0})	d experimental (A^{0})
100	3.5861	3.626
110	2.0705	1.810
200	1.7931	1.810

Figure 1. A) TEM image of CdS triangular shaped nanocrystals. B) HRTEM of a nanocrystal. C) PS of this nanocrystal

Scanning Electron Microscope

(SEM)

Figure 2. SEM image of CdS nanoparticles

Electrical transport studies

1 Electrical Conductivity

Variation of dc conductivity σ_{dc} and ac conductivity σ_{ac} of CdS with temperature is shown in figure 3. The log σ_{dc} vs 1000/T graph of CdS shows two distinct regions, the first region indicating a slow increase of conductivity with temperature and the second one indicating a rapid increase beyond this temperature. σ_{ac} of CdS samples is found to increase linearly with frequency. Ac conductivity σ_{ac} increases at a low rate with temperature initially and more rapidly beyond about 425K. The σ_{ac} versus 1000/T graphs of the samples at low frequencies show a maximum around almost the same temperature. The variation of dielectric constant Є and the ac conductivity σ_{ac} of the CdS samples as function of temperature is shown in figure 4.

It is clear from the present study that the dc conductivity of CdS increases at a lower rate or is approximately constant up to 500K and thereafter the conductivity increases at a rapid rate. Beyond Tc it is seen that the portion of the σ_{dc} versus 1000/T is almost a straight line showing an Arrehenious behaviour. The lack of dependence of conductivity on temperature up to Tc may be attributed to the large band gap (nanosize), due to which the charges are not released from the particles by thermionic emission are not available for tunneling. The conductivity above Tc is due to both thermionic emission and tunneling of charge carriers across the barrier. Because of the small size of the particles, the charge carriers reach the surface of the particles more easily enabling easy electron transfer by thermionic emission, or tunneling or both, enhancing the conductivity

The dielectric constant of nanoparticles of CdS is found to be larger than the corresponding values of CdS crystals [30, 31]. Also σ ac of CdS is much larger than that

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of the bulk crystals [32, 33].Unlike the case of ionic crystals, where the effective fields CdS nanocrystalline were synthesized using thiophenol as capping agent. By changing the relative ratio of sulphide to thiophenol, clusters of different sizes were obtained. Electrical and optical properties of CdS nanocrystallites exhibit extraordinary behavior over that of bulk.

$$E_{eff} = E + (4/3) \, \text{л} \, P,$$

For semiconductors E_{eff} should be essentially equal to the macroscopic field E,

i.e. $E_{eff} = E$.

This leads to an expression for Є of the form $\text{Є} - 1 = 4\text{л}\alpha/V$ where V is the volume. The large value of Є of pallets of nanoparticles of CdS compared to the corresponding bulk values may due to the small of V in the above expression. The very large value of σ_{ac} of CdS may be attributed to the defect structure of the particles [34, 35].
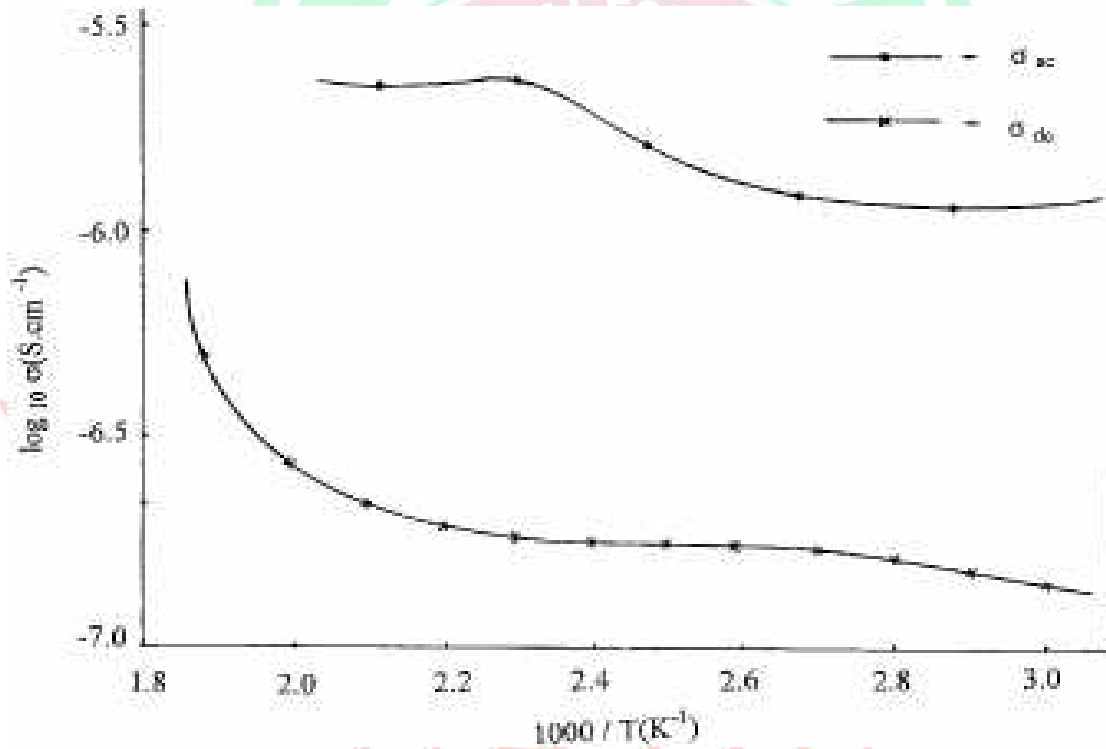

Figure 3. Variation of log of dc conductivity σ $_{dc}$ and ac conductivity σ $_{ac}$ of CdS with 1000/T.
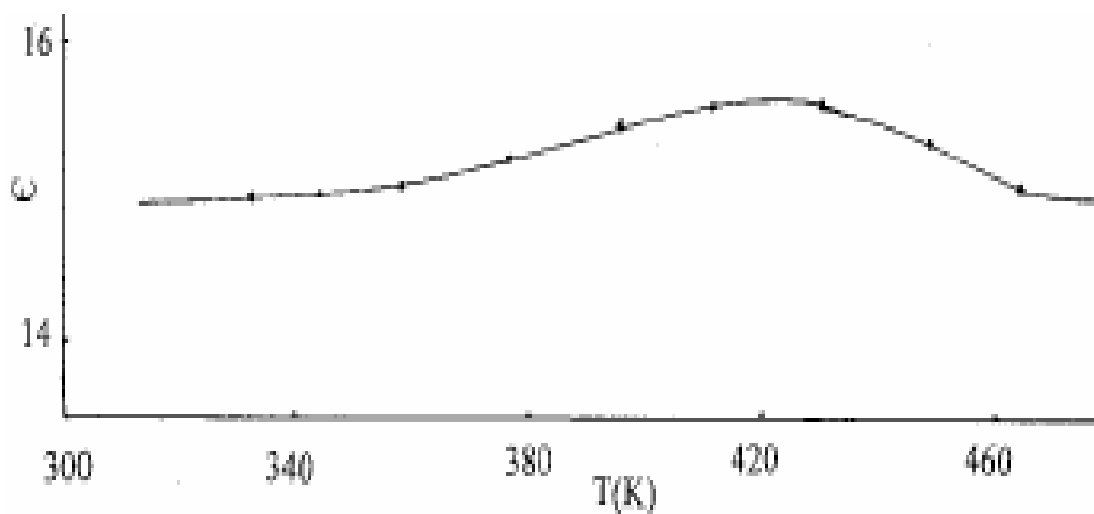
Figure 4. Variation of dielectric constant Є of CdS samples with temperature

Result & conclusion

The basic principle of sol-gel technique is to make a solution of the elements of desired composition in an organic solvent, polymerize the solution to form gel then it is decomposed in the substrate in a spin coater with in definite speed of rotation to form a uniform thin films.

The XRD pattern of CdS nanoparticles showed the materials to be of the nanometric size regime with a predominantly cubic phase. It was shown that the sizes of nanoparticles are 30-40 nm, which confirms from SEM.

AFM analysis of a film shows that the surface is composed of crystallites with an approximate size of 30 nm grouped together into larger agglomerates.

The transmission electron microscopy (TEM) pattern shows that most of the particles are characterized by an angular shape with an average size of 10 nm. To determine the structure of isolated triangular nanocrystals, high-resolution transmission electron microscopy (HRTEM) experiments and image processing by the square Fourier transform (power spectrum, PS) are performed. The HRTEM image of the triangular nanocrystals shows several lattice planes. The PS shows several well defined sharp spots:

The log σ_{dc} vs 1000/T graph of CdS shows two distinct regions, the first region indicating a slow increase of conductivity with temperature and the second one indicating a rapid increase beyond this temperature. σ_{ac} of CdS samples is found to increase linearly with frequency. Ac conductivity σ_{ac} increases at a low rate with temperature initially and more rapidly beyond about 425K. The σ_{ac} versus 1000/T graphs of the samples at low frequencies show a maximum around almost the same temperature.

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