



SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE CdS THIN FILMS

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Abstract

The study of semiconductor nanoparticles has been an interesting field of research for more than two decades. The confinement effect is observed for CdS particles when the particle sizes are equal to or less than 50 Å . 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. The optical properties of CdS nanoparticles have been extensively studied in recent years as this material exhibits pronounced quantum size effects. The present work 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. To accomplish this aspiration, the entire research work is divided into two parts. At the

beginning, efforts have been made to optimize the deposition conditions. It is needless to mention that the properties of the thin films depend extensively on the growth conditions, which influences its microstructure. Different parameters like substrate temperature, PH of solution, deposition time, speed of rotation etc. were carefully monitored to decide the optimized growth condition of the thin films.

Kewwords: nanocrystalline CdS, sol-gel.

Introduction

Semiconductor nanocrystals exhibit a wide range of size-dependent properties. Variations in fundamental characteristics ranging from phase transitions to electrical conductivity can be induced by controlling the size of the crystals. The properties of crystalline solids are ordinarily catalogued without reference to their size. It is only in the regime below 10 nm where this variable comes into play. In the past decade, tailoring of materials characteristics by size control has been demonstrated in many inorganic solids belonging to one of the most technologically important classes of materials: semiconductors. For example, in the prototypical material, CdS, the band gap can be tuned between 2.5 and 4 eV, while the radiative rate for the lowest allowed optical excitation ranges from several nanoseconds down to tens of picoseconds [1]. The energy above the band gap required to add an excess charge increases by 0.5 eV [2], while the very notion of charge transport no longer seems to apply. The melting temperature varies from 1600 down to 400 °C [3]. The pressure required to induce transformation from a four- to a six-coordinate phase increases from 2 to 9 GPa, even as the number of nucleation events for the transition becomes one [4]. This enormous range of fundamental properties is all realized in a material of a single chemical composition: CdS. The variation is achieved by reducing the size of the crystal, not by altering its chemical composition. There are two major effects which are responsible for these size variations in nanocrystal properties. First, in nanocrystals the number of surface atoms is a large fraction of the total. Second, the intrinsic properties of the interior of nanocrystals are transformed by quantum size effects. In any material, surface atoms make a distinct contribution to the free energy, and the large changes in thermodynamic properties of nanocrystals (melting temperature depression, solid-solid phase transition elevation) can ultimately be traced to this. Then surfaces of nanocrystals have until recently been thought of as largely disordered, yielding spherical or ellipsoidal shapes [5]. More recent work shows that nanocrystals assume regular shapes, with the same well-defined facets as are

present in extended crystals[6,7]. This opens up the possibility of manipulating the surface energetics of nanocrystals in a controlled manner. The ability to manipulate the energetics of nanocrystal surfaces at will would have practical consequences. To date, nanocrystals are observed to occur in the same crystal structure as the extended solid [8] It remains an open question whether it will be possible to prepare nanocrystals with interior bonding geometries that do not occur in the known extended solid, by appropriately adjusting the surface energy. Thus, nanocrystals with entirely distinct properties from their extended counterparts may be envisioned [9]. The first part of this review will cover issues related to phase transitions in nanocrystals, with the goal of understanding whether such novel bonding geometries may be stabilized. The second part of the review will cover what is known about the structure and composition of colloidal semiconductor nanocrystal surfaces. Independent of the large number of surface atoms, semiconductor nanocrystals with the same interior bonding geometry as a known bulk phase often exhibit strong variations in their optical and electrical properties with size [10, 11]. These changes arise through systematic transformations in the density of electronic levels as a function of the size of the interior, known as quantum size effects. Nanocrystals lie in between the atomic and molecular limit of discrete density of electronic states and the extended crystalline limit of continuous bands. Now in any material, there will be a size below which there is substantial variation of fundamental electrical and optical properties with size, which will be seen when the energy level spacing exceeds the temperature. For a given temperature, this occurs at a very large size in semiconductors, as compared to metals, insulators, and van der Waals or molecular crystals. This can be understood by considering that the bands of a solid are centered about atomic energy levels, with the width of the band related to the strength of the nearest neighbor interactions. In the case of van der Waals or molecular crystals, the nearest-neighbor interactions are weak and the bands in the solid are very narrow, and as a consequence not much size variation in optical or electrical properties is expected or observed in the nanocrystal regime. As a function of increasing size, the center of a band develops first and the edges develop last. Thus, in metals, where the Fermi level lies in the center of a band, the relevant energy level spacing is still very small, and at temperatures above a few kelvin, the electrical and optical properties more closely resemble those of a continuum, even in relatively small sizes (tens or hundreds of atoms)[12] In semiconductors, however, the Fermi level lies between two bands, so that the edges of the bands dominate the low-energy optical and electrical behavior. Optical excitations across the gap depend strongly on the size, even for crystallites as large as 10 000 atoms. The electrical transport properties of nanocrystals also depend strongly on size. The energy required to

add successive charges onto an extended crystal does not vary. In a nanocrystal, the presence of one charge acts to prevent the addition of another. Thus, in metals or semiconductors, the current-voltage curves of individual crystallites resemble a staircase, due to this “Coulomb blockade [13]”. Steps in the staircase due to individual charging events are spaced proportional to $1/\text{radius}$. These effects have been studied extensively in lithographically prepared semiconductors with lateral dimension of $0.1 \mu\text{m}$ and in some metal nanocrystals [14]. The electrical characteristics of individual semiconductor nanocrystals, in which Coulomb blockade effects and discrete energy level spacings are both expected to occur, are a topic of much current research [15].

Materials and Methods

Synthesis of nano CdS

Cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and thiourea ($\text{SC}(\text{NH}_2)_2$) in a molar ratio of metal salt / $\text{SC}(\text{NH}_2)_2 = 1/2$ were dissolved in MeOH and then proper amounts of these methanol solutions were mixed with the above solutions. The solutions thus prepared were kept at around 50°C for gelation. The resultant gels containing thiourea complexes were heat-treated in air for the elimination of residual organics and the decomposition of the complexes to sulfides. CdS film is of yellowish Orange colour

The substrate

Nanocrystalline thin films of CdS were deposited on glass substrates

Substrate cleaning

Before loading, the substrates were cleaned in the sequences: TCE (Tri -Chloro-Ethylene), Acetone and Methanol. Samples were immersed in the respective chemicals in boiling condition, for 5 minutes in each chemical in the sequence mentioned above to remove the organic contaminations from the substrate surface.

Deposition of CdS thin films

A solution of CdS precursor is deposited on a glass substrate by a single wafer spin processor (Lawrell Technology Corporation, Model WS-500-6NPP/LITE). After setting the substrate on the disk of the spin coater, the coating solution approximately 0.2 ml was dropped onto glass substrate which was rotated at 4000 rpm for 30 s. After deposited by spin coating, the films were dried at 50

$^{\circ}\text{C}$ for 15 min to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated 5 times until the desired thickness of the films was reached.

Thickness measurements were performed with a Stylus Profiler (Tencor P10). The total thickness of the films was in the range of 500–650 nm. Then the films were inserted to a furnace and annealed at 100–200 $^{\circ}\text{C}$ for 30 min.

Figure. shows the flow diagram for nano CdS films prepared from the sol-gel process using the spin-coating method.

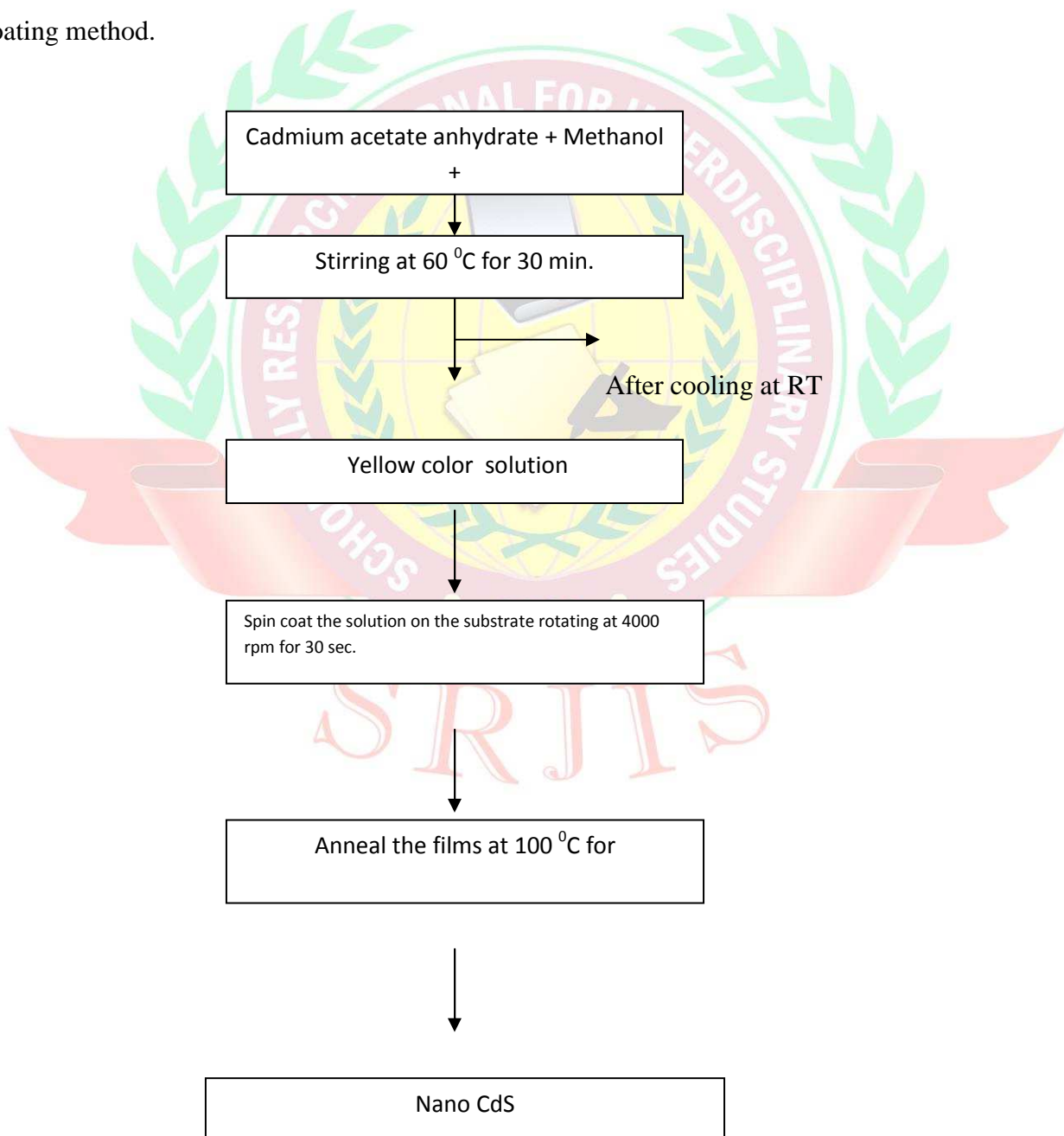
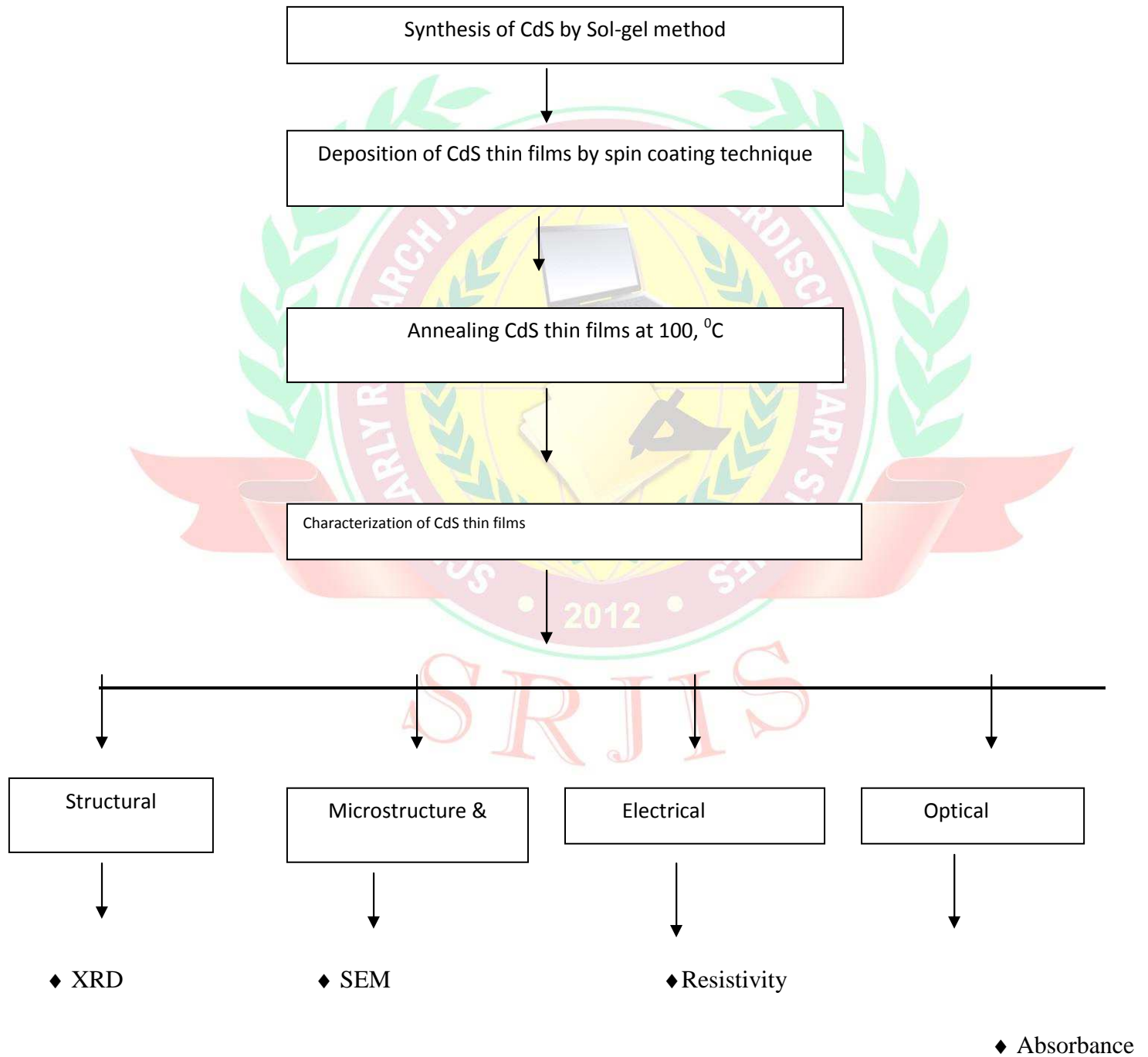


Figure 1. Flow diagram shows the synthesis route of Nano CdS thin films using sol-gel method



◆ AFM

Figure 2. **Flow diagram of synthesis and characterization of Nano CdS thin Films**

Structural studies

1.1 X-ray diffraction

The XRD pattern of the precipitated nanoparticles was illustrated in Fig. 3. It can be attributed to hexagonal CdS (JCPDS – file No. 10-0454). The broadened peaks are indicating that the sizes of the particles are in nanorange. In order to achieve more confirmative information, the Debye–Scherer formula [72];

$$L = 0.9\lambda / B \cos\theta = 34 \text{ nm}$$

has been applied to calculate the size of the nanoparticles. Here, L is the coherent length, λ is the wavelength of X-ray radiation, B is the full-width at half-maximum (FMWH) of the peak, and θ is the angle of diffraction. In the case of spherical crystallites, the corresponding crystallite size of nanoparticles obtained in this way is 34 nm which confirms our findings in SEM image

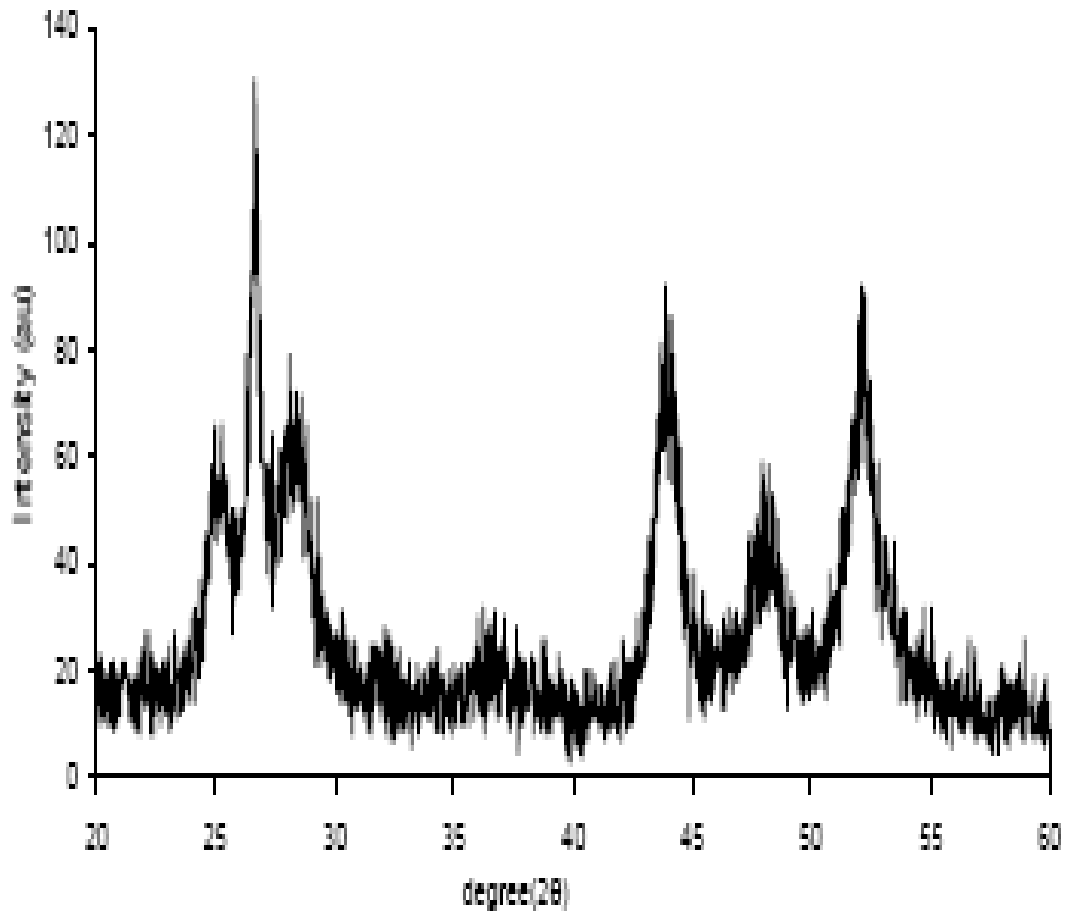


Figure 3. XRD pattern of CdS nanoparticles.

2. Microstructure and Morphological studies

2.1 Atomic Force Microscope (AFM) of nano CdS

AFM analysis of a film (Fig. 4) shows that the surface is composed of crystallites with an approximate size of 20 nm grouped together into larger agglomerates, the RMS surface roughness is found to be 4.4 nm.

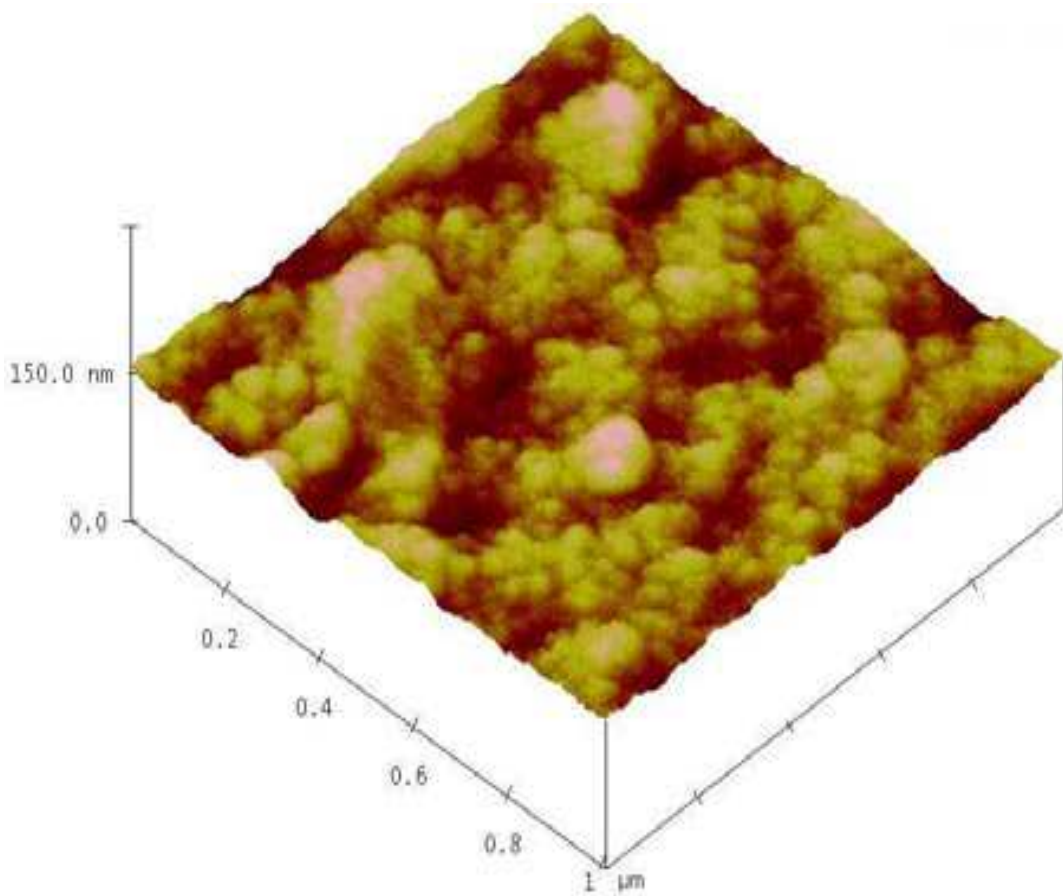


Figure 4. AFM image of as-grown CdS film. Sample area is $1\mu\text{m}$ by $1\mu\text{m}$

2. Characterization of thin films

2.2.1 Structural analysis

The structural properties of the films were investigated by X-ray diffraction (XRD) (Philips PW-3710, Holland) was carried out using filtered Cu $K\alpha$ radiation ($\lambda = 1.54056$) operated at 40 kV, 20 mA, The scanning range is from 20° to 60° and the scan rate is $2^\circ/\text{min}$ ($0.04^\circ/\text{sec}$).

2.2.2 Microstructure and Surface morphology

The surface morphology was investigated using atomic force microscope (AFM, SPA-300HA). The surface and cross-sectional morphologies of the films were observed by (SEM) using a Quanta-200, Holland. A thin layer of gold ($\sim 100\text{nm}$) was sputtered on the film to avoid the charge

build up. The microstructure was observed on the top surface of the film as well as the cross section of the film. The thickness of the film was determined using cross section of SEM.

2.2.3 Electrical measurements

D.C. conductivity was determined by measuring the resistance of the sample using an electrometer in the V/I mode. Dielectric constant ϵ and ac conductivity σ_{ac} , of the samples were determined using an impedance analyzer over a frequency range 10kHz to 13MHz

2.2.4 Optical measurements

In order to study the optical properties of CdS nanocrystallites, we have characterized these samples through optical absorption, photoluminescence, luminescence decay and photovoltaic measurements.

The optical absorption spectra of CdS thin films were measured using a double-beam spectrophotometer Shimadzu UV-140 in the 300-1000nm-wavelength range.

Result and discussion

Nanocrystalline semiconductor materials such as CdS have attracted considerable attention due to their unique properties, which are not present in bulk materials. These nanoparticles exhibit size dependent properties (size quantization effects) such as a blue shift of absorption onset, a change of electrochemical potential of band edge, and an enhancement of photocatalytic activities, with decreasing crystallite size. CdS, in particular, have been extensively studied due to their potential applications such as field effect transistors, light emitting diodes, photocatalysis and biological sensors. Many synthetic methods have been employed to prepare CdS nanoparticles including soft chemical reaction, solid-state reaction, sonochemical preparation, microwave heating, photoetching and reverse micelle. In this investigation, we have developed a new method to produce CdS nanoparticles of small sizes using sol gel process.

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.

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