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Growth of limited quantum dot chains of cadmium hydroxide thin films by chemical route

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Abstract

A nanocrystalline $Cd(OH)_2$ thin film composed of linked (3–4) quantum dots was prepared on a indium-tin oxide coated glass substrate by low temperature chemical process using two different precursor solutions. The structure of the chains was characterized by XRD, SEM, and UV–Vis spectrophotometer. As-deposited $Cd(OH)_2$ thin film was 205 nm thick and composed of loosely packed quantum dots chains with each of 20–30 in diameter and (chain) length of 80–90 nm, respectively.

Keywords: $Cd(OH)_2$ quantum dots; XRD; SEM

In recent times, nanoclusters of metals and semiconductors are more and more being considered as the building blocks of the future modern technologies. This is due to the size dependent electronic properties of these materials. Ultra-fine particles are used in surface chemical, photochemical and other fields. Cadmium hydroxide, $Cd(OH)_2$ is a wide band gap semiconductor with a wide range of possible applications including solar cells, photo transistors and diodes, transparent electrodes, sensors, etc. [1,2]. These applications of cadmium hydroxide are based on its specific optical and electrical properties. For example, these films show a high transparency in the visible region of the solar spectrum, as well as high ohmic conductivity. The intensity of optical and electrical effects of these films depends on the deviations from the ideal cadmium hydroxide stoichiometry, as well as on the size and shape of the particles. Within the physical science community several investigations on the fabrication of cadmium oxide nanostructures and the optimization of their optical performance have been carried out in the past few years [3–6] but very less attention has been focused on cadmium hydroxide.

We wish to report here evolution of a new morphology of cadmium hydroxide films consisting of limited quantum dot chains in a nanometer scale by self-assembled layer-by-layer deposition. Each limited (length) chain of cadmium hydroxide is composed of 3–4 quantum dots shows strong evidence of quantum confinement when compared to bulk cadmium hydroxide optical properties [7,8].

For the deposition, extra pure chemicals such as Acros made cadmium chloride and ammonia from Samchun Pure and Chemical Co., were used. Triply distilled water was used as a solvent. For the preparation of $Cd(OH)_2$ thin films. All the above-mentioned chemicals were initially stored in *vacuum* for about 12 h before use. Solution of cadmium chloride (0.1 M) was prepared at room temperature, and its pH was adjusted to 9 by addition of ammonia water. This cadmium solution was maintained at room temperature whereas water at 75 °C using accurate temperature controller unit. Precleaned commercial indium-tin oxide (ITO) glass slide served as substrate. When ITO substrate dipped in a

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cadmium chloride solution, there is heterogeneous reaction between the solid phase of the substrate and the solvated ions in the solution. After 15 s, the ITO substrate was taken out and then immersed in water for 10 s. There is heterogeneous chemical reaction at the solid interface between the adsorbed cations $[Cd(NH_3)_4]^{2+}$ and anions ($2OH^-$). One cycle consists of immersion of substrate in cadmium chloride solution and water. After 20 cycles, a thin whitish film of $Cd(OH)_2$ was formed on ITO substrate. The film was washed with deionized water, dried, ultrasonically cleaned and used for further studies. Limited quantum dot chains of cadmium hydroxide were structurally characterized under high resolution scanning electron microscopy (SEM, JEOL) with an accelerating voltage of 15 kV. It is no doubt that SEM gives a more accurate result on the morphology of obtained cadmium hydroxide films. The cadmium hydroxide film was coated with a 10 nm platinum layer using polaron scanning electron microscopy sputter coating unit, before taking micrograph. X-ray powder diffraction operated under the conditions of 40 kV and 100 mA with Cu-Kα radiations (λ = 1.5426 Å). Two hundred and five nanometer thickness of deposited cadmium hydroxide thin film was measured by ellipsometry method by using constant refractive index of the single crystal Si sample. The nominal growth rate of $Cd(OH)_2$ thin film on ITO substrate was 7–8 nm/cycle for first few cycles which was later drastically increased to 14–15 nm/cycle. At initial stage, the low average nominal growth rate may be caused by formation of $Cd(OH)_2$ nuclei at preferential area of ITO substrate. Relatively easy attachment of new form $Cd(OH)_2$ quantum dot on pre-formed results into increase in average growth rate. Multiple layers of cadmium hydroxide of the limited chains are laid down on the ITO substrate.

In the first stage, the ammonia complexed cadmium ions $[Cd(NH_3)_4]^{2+}$ are adsorbed ITO surface. In second step, hydroxide ions from water react with the adsorbed cadmium species as

$$[Cd(NH_3)_4]^{2+} + 2H_2O \rightarrow Cd(OH)_2 + 2NH_4^+ + 2NH_3 \quad K_{sp} = 5.27 \times 10^{-15} \tag{1}$$

Fig. 1 shows typical X-ray diffraction (XRD) pattern of cadmium hydroxide thin films and ITO as a reference. Pattern of cadmium hydroxide shows a good degree of crystallinity. The location of patterns corresponding to cadmium hydroxide such as (0 2 0), (0 1 1), (1 5 0), (2 4 0), (0 0 2), (0 6 0), (1 0 2), (3 3 1) and (0 7 0) are in good agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) reference diagrams for the corresponding bulk phases [20-0179] with lattice constants a = 5.63 Å, b = 10.18 Å, and c = 3.40 Å, respectively. To obtain more quantitative information, the XRD pattern was convoluted with Guassian function whose full width at half maxima was determined from the Debye–Scherrer formula. It is reported [9] that the Debye–Scherrer relationship is a good approximation only for a spherical crystal; the size is inversely proportional to the full width at half maxima. To be more precise, the value of full width at half maxima depends on the length over which the periodicity of the crystal is complete. Plane (0 2 0) was used to determine average grain size of $Cd(OH)_2$ quantum dot was 30 nm. For other peaks the average value of grain size falls between 20 and 30 nm.

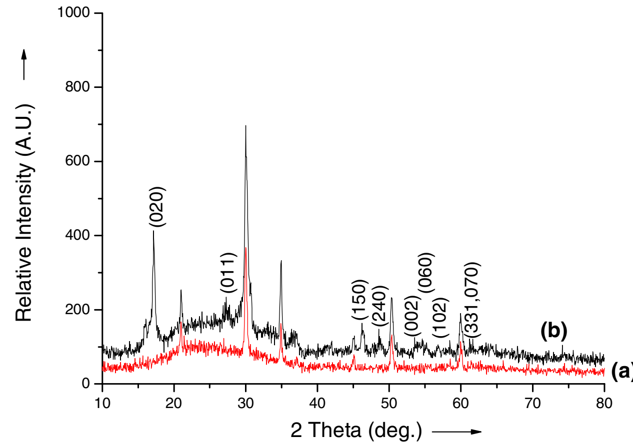

Fig. 1. XRD spectra of (a) bare ITO and (b) $Cd(OH)_2$ thin films. Well-defined peaks corresponding to $Cd(OH)_2$ are clearly seen.

SEM image (Fig. 2) shows uniform chains of cadmium hydroxide quantum dots with average diameter 20–30 nm and average length 80–90 nm. Images show smooth surface morphology under lower (a) and higher magnifications (b). Film surface with coalesced grains is seen clearly. Strong non-preference for self-assembly of these chains with three to four quantum dots, in which they align with their long axis non-parallel to each other, is observed. Inset of Fig. 2(a) shows a selected region of $Cd(OH)_2$ thin films consisting of three to four typical chains composed of 3–4 quantum dots together. This feature may be useful when considering for optical applications of bulk and dependent quantum dots of cadmium hydroxide. Energy dispersive X-ray analysis recorded (not shown) while SEM image shows a 1:2 Cd:OH composition that is consistent with stoichiometric $Cd(OH)_2$, revealing that the quantum dot chains are composed of pure $Cd(OH)_2$ and not CdO. It can be observed that cadmium hydroxide limited quantum dot chains are uniform, homogeneous and well cover the substrate without any voids, pinholes and cracks. Films were found to be thermally and physically stable, without degradation even at temperature 100 °C as there was no noticeable phase change recorded with XRD and SEM studies when exposed to environment for couple of days.

We performed optical studies of this limited chains of cadmium hydroxide to determine the potentially un-