Galvanic-fabrication of CdS microstructures using nuclear track filter membranes

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Ordered or regimented arrays of nanostructures are potential vehicles for implementing a large number of high performance electronic, magnetic, optical, and multifunctional devices and sensors. Materials with nanoscopic dimensions not only have potential technological applications but are also of fundamental interest in that the properties of materials can change in this regime of transition between the bulk and molecular scales. Many reviews are available on the synthesis of nanostructured materials (NSMs) involving materials such as metals and non-metals such as semiconductors, polymers, glasses, carbon etc. [1, 2]. The advancements in the development of semiconductor nanoparticles and clusters (ca. 1 to 20 nm), often referred to as quantum dots, Q-particles and nanocrystals, have been very rapid [3]. Most of the semiconductors being synthesized chemically belong to the group II–VI, IV–V and III–V binary systems as well as ternary diluted magnetic semiconductor clusters. There are many methods for synthesizing these semiconductor clusters which exist in the form of dispersed colloids; trapped and stabilized within micelles, polymers, zeolites, glasses, etc. [4, 5].

CdS, one of the well-known photonic materials, has been synthesized as clusters by adopting mimic organic polymerization reactions as synthesis strategy. Stabilised CdS nanoclusters in solid thin-film form have also been synthesized by using a polymer as a matrix [6, 7]. Herron *et al.* [8] have reported synthesis of $a \sim 15$ A single size tetrahedral CdS cluster. Excellent reviews on various methods and techniques for chemical synthesis of CdS and other semiconductor clusters and nanoparticles are available in the literature (see, for example, refs.1–2).

Another novel technique, known as the technique of "Template Synthesis" (TS) [9] based upon the electrochemical technique of galvanic replication, has also been used to synthesize semiconducting compound materials. Rectifying metal-semiconducor diodes (II-VI semiconductors) and Resonant Tunneling Diodes (RTDs) (metal-semiconductor Cu-Se system) fabricated through this technique have also been reported [10–12]. Klein *et al.* [10] synthesized high spatial density ($>10^9$) II–VI semiconductors CdSe and CdTe (cadmium chalcogenide) microdiode arrays. We report here for the first time the generation of CdS microstructures through the use of this technique based upon the galvanic replication of high density and high aspect-ratio etched cylindrical channels in Nuclear Track Filters (NTFs) of Makrofol (poly-carbonate).

The TS technique entails synthesis of desired materials (metals, semiconductors, polymers, metal-semiconductor junctions) of very low dimensions-down to a few nm. The underlying principal of the technique used is well known; it is an electrochemical process in which ions in a supporting solution are reduced to the solid state at the cathode which, if overlaid by an NTF, would lead to the growth of an electroplated film; the microstructures and nanostructures, depending upon the size of the etched pores, acting as templates. The generated structures can both be heterogeneous (including multilayered), short, squat fibrils, long needle-like fibrils, tubules, tapered conical (single or double cones), elements, etc. depending on the pore size (nano/micro) and geometry, with complete control over the aspect ratio possible. The technique is very simple, yet graphite nanotubules with extraordinary low dimensions (ca. 3 nm) have been reported to be generated [13]. Bandyopadhyay and Miller [14] have also discussed the technique of filling the pores by electrodeposition. As is evident, the TS is membrane based technology. One of the types of membranes being used here is known as Track Etch Membrane or Nuclear Track Filter (NTF). NTFs have emerged as a spin-off from solid state nuclear track detectors (SSNTDs)-solid dielectric materials capable of storing tracks of energetic, heavily ionizing ions which can subsequently be chemically amplified as see-through pores or channels of well defined geometry and spatial density. NTFs have been put to numerous filtration applications besides their use in the synthesis of nano/microstructures and devices [15–17]. Martin [17] and Chakarvarti and Vetter [16, 18] have produced extensive reviews of the TS technique alongwith morphological revelations of the structural ensembles so generated. The TS of semiconductors is usually carried out using the galvanic replication technique by applying the synthesis process to a metallic cathode substrate which is closely covered by an etched NTF as an overlay and has custom-made pores which act as templates for growth of structure. In general, a suitable cell design is required and the layout design of such a cell along with other relevant details of the technique has been discussed previously [16].

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The NTF used here as template was of Makrofol KG foil (polycarbonate from Bayer AG), 10 μm thick, having an average pore diameter $\sim$2 μm with pore density 2×10^9 m^{-2}. This was prepared by irradiating the foil with Si^{8+}, energy ca. 100 MeV at 90° at the GPSC of the Pelletron at the Nuclear Science Centre (NSC), New Delhi, India, followed by chemical amplification of the damage trails by etching in 6 N NaOH, at 50 ± 2 °C for 35 min. In order to produce see-through pores, optimum etch time and etch conditions are pre-set. For the fabrication of the CdS microstructures in the form of columnar ensembles, the cathode (Al tape as substrate having its base coated with conducting adhesive) of the specially designed elctrodeposition cell, having provisions for temperature control and stirring at different speeds [19], was covered closely with the processed NTF and the electrolyte solution to be used in the bath was prepared using milli Q 10-MΩ water and ultrahigh purity reagents 0.002 M $3CdSO_4 \cdot 8H_2O(98\%) + 0.1$ M Na_2SO_3 (99.9%). The pH of the electrolyte was adjusted to 2–3 using dilute H_2SO_4. The galvanic replication was carried out for 50 min at 3.5 V (current 0.037 to 0.078 A) at a room temperature of 29 ± 1 °C with an anode of pure Cd. The optimum conditions e.g., temperature, voltage, time, stirring, etc. depend upon the cell dimensions, chemistry of the process and previous experience [16]. After the plating process was completed, the NTF overlay alongwith the substrate was removed and the Makrofol foil was dissolved carefully in CH_2Cl_2 so that the grown microstructure with Al as substrate or a platform is revealed. Fig. 1 shows SEM photograph displaying the top view of the synthesized microstructures.

Earlier it has been reported that if the dimensions of the pores were small, it would suppress the fractal-like cauliflower morphology, which is a usual feature in electrodeposited II–VI materials [10, 20]. In the present case, a close view of the microstructures depicting the typical cauliflower morphology of the synthesized CdS microstructures is obtained and shown in Fig. 2. This is expected because of the fact that the pore size here was not in the nanorange. It has been reported [see ref. 14] that bright field high resolution transmission electron microscopy of the materials deposited in the pores show a crystalline structure and crystallinity can further be increased by thermal annealing. Further studies on optoelectronic properties of such microensembles of CdS are being carried out.

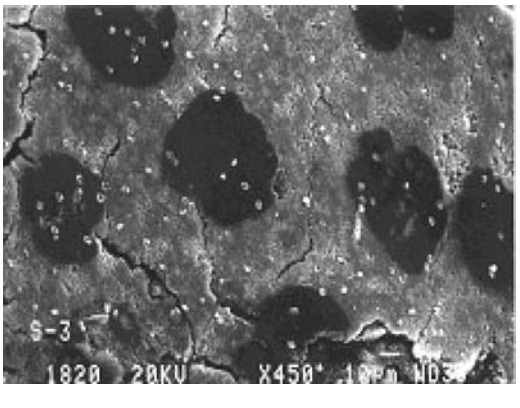

Figure 1 Scanning Electron Microscope top view image of syntesized CdS microstructure using the technique of template synthesis. Microensemble is shown in the form of dots.

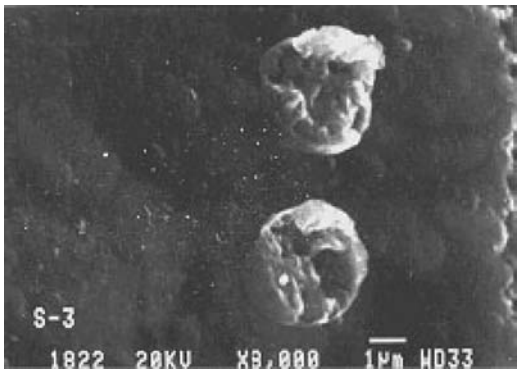

Figure 2 Fractal-like cauliflower morphology of CdS microstructures.

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