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ELECTROCHEMICAL SYNTHESIS AND LASER INDUCED TIME RESOLVED LUMINESCENCE BEHAVIOUR OF CdSe NANOWIRES

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In this paper, we report the fabrication of CdSe nanowires using electrochemical technique known as Template Synthesis with polycarbonate ion-track membranes having nanopores as templates, and their luminescent behavior. Scanning electron microscopy was used for morphological studies of CdSe nanowires. For optical studies, UV laser induced photoluminescence behaviour was investigated using pulse excitation method. Emission was found in the visible region and lifetimes were in the microsecond time domain.

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1. Introduction

There is continuous interest to the production and investigation of one dimensional nanowires mainly due to their prospective innumerable applications in diverse fields including magnetic, electronic and optical devices [1-2]. There are many procedures used in the production of nanowires but the template synthesis (TS) is elegant, adaptable and cost-effective for production of the variety of nanomaterials including metals, semiconductors, hetero-junctions, conducting polymers, CNTs etc [3,4 and references therein, [5-7].

CdSe is one of the II-IV semiconductors and because of elevated photo-sensitivity, it has been extensively used in photoconductive devices [8-10]. CdSe nanowires have been produced by direct current (dc) as well as alternating current (ac) electrodeposition into the pores of Anodic alumina membrane(AAM) using $CdSO_4$ and Se dissolved in DMSO (dimethyl sulfoxide) at high temperature [11]. CdSe nanowires have also been synthesized through the pores of AAM from alkaline solution containing $CdCl_2$ and SeO_2 by electrochemical deposition at room temperature [12]. Highly specific conditions like concentration, pH and cathode potential are requisites to have fine stoichiometry ratio for Cd and Se.

CdSe nanowires have also been produced by MOCVD technique [13], pulsed laser deposition technique [14], vapour-liquid-solid (VLS) technique [15], solution-liquid-solid (SLS) technique [16], sublimation of CdSe powders [17]. A non-galvanic method (chemical method) for preparing an ordered and crystalline array of CdSe nanowires using AAM as template has also been reported [18]. In the present paper, pores in ion track membranes were used as templates for the synthesis of CdSe nanowires using simple dc electro-deposition technique at 75±5ºC. The electrochemical deposition is a route which involves charge transfer, diffusion, reaction and adsorption. Consequently, the formation of nanowires is strictly related to deposition parameters [19].

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2. Experimental

For CdSe deposition, 8 µm thick polycarbonate membrane (Whatman) with 80 nm diameter pores with a pore density of 10^8 cm^{-2} has been used. In general, a suitable cell with proper lay-out design is required[4]. In the present case, two electrode cell made of Teflon was used. The electrolyte solution consisted of 0.05M $3CdSO_4.8H_2O$ and 0.1 Na_2SeO_3. Deionized water was used for preparing the solution. The pH of solution was kept 2.5 using diluted H_2SO_4.

The galvanic replication was carried out for 50 min at 2 V (current 0.017 to 0.031 A) at 75±5ºC 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. After the deposition, the polycarbonate templates with CdSe nanostructures were immediately removed from the electrolyte, first rinsed with double-distilled water and ethanol and then dried in air at room temperature. The porous polycarbonate membrane was removed by dissolving it in dichloromethane followed by several washings with double-distilled water.

The cleaned and dried samples were coated with a layer of gold-palladium alloy in Jeol, Fine Sputter JFC 1100 sputter and subsequently mounted on specially designed aluminum stubs using double-sided adhesive tape. The samples thus mounted were viewed under Jeol, JSM 6100 scanning microscope at an accelerating voltage of 20 kV. Figure1 shows the SEM micrographs of the CdSe nanostructures.

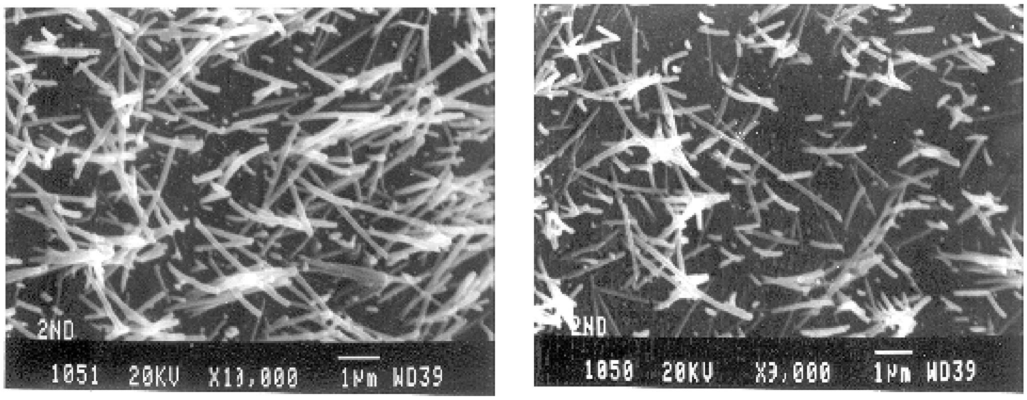

Fig. 1. SEM micrographs of the CdSe nanostructures

Laser induced pulse excitation method was used to study the PL spectra. Nitrogen laser is the most suitable excitation source (337.1 nm) to irradiate the CdSe nanostructures having pulse-width of 5-7 ns and average power of 10 kW and peak power of 1 MW. High photon flux density of the nitrogen laser is extremely useful to excite the short-lived shallow trapping states. The short-lived phosphorescence from the sample(Fig-2) at an angle of 90° to the incident beam was collected by a fast photo-multiplier tube through an assembly of monochromator and PMT tube. The decay signals (Fig-3) from the CdSe nanowires were recorded by digital storage oscilloscope (TDS-1012) and analyzed using computer simulations so as to calculate the excited state lifetimes of the nanowires.

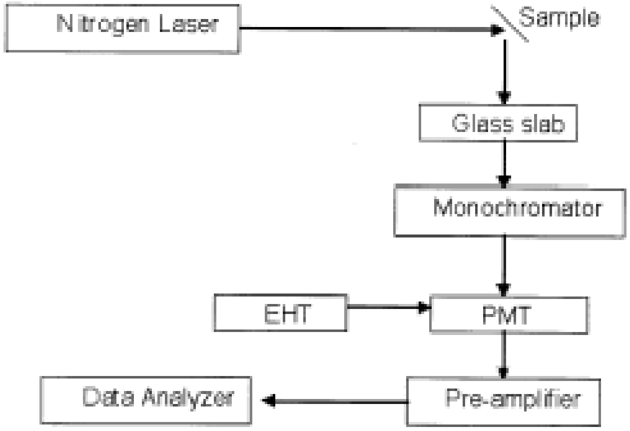

Fig. 2. Photoluminescence setup

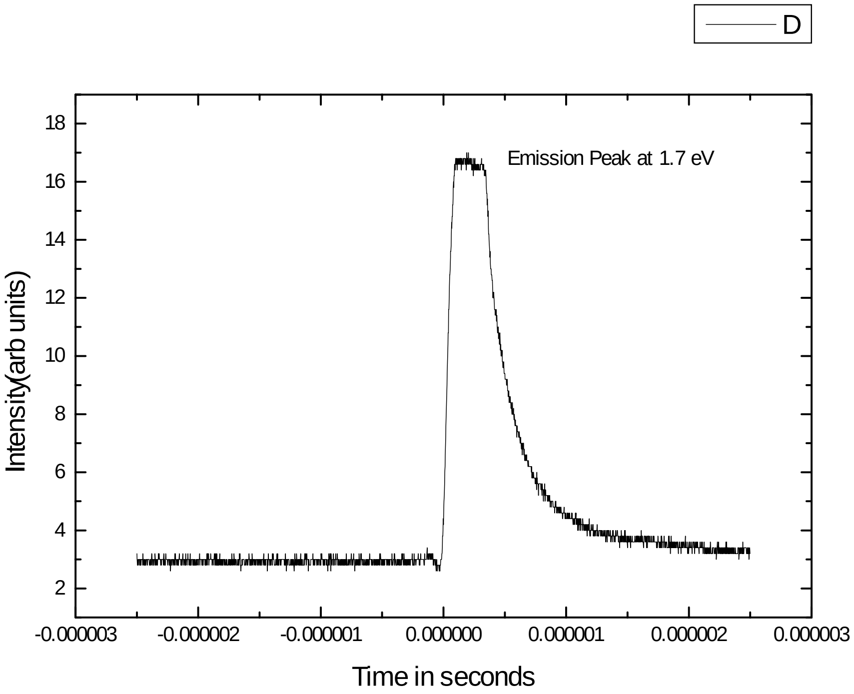

Fig. 3. Time resolved photoluminescence decay curve of CdSe nanowires

3. Results and discussion

In the present work, we used the ion track membranes (Whatman) of thickness 80 nm. Due to their precise physical properties, cadmium chalcogenides such as CdTe, CdSe, and $CdSe_xTe_{1-x}$ are semiconducting compounds that can be used beneficially in various applications and, in particular, for the possible applications in photovoltaics or photo-electrochemical cells.

The electrolyte composition, pH and the temperature effects on the deposition time, microstructure, crystalline orientation and surface composition of chalcogenide films also have been reported in detail [20].

The Laser induced photoluminescence studies reveal that the CdSe nanowires are luminescent in nature. Hyperbolic decay curves are observed in the case of CdSe nanowires. From the decay curve we can separate multiple exponential curves and we can find out excited state the lifetimes. The emission wavelength is in the visible region and the peak is observed at around 1.7 eV (Fig-3) and the lifetime values are in the microsecond time domain. The micro-second time domain of the transitions shows that the optical decay is due to the weak electric dipole transitions. The luminescent properties of these nano wires, make them useful for various applications.

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