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Template synthesis and morphology of CdS nanowire arrays using anodic alumina membranes

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Abstract

It is well known that template synthesis is a simple and versatile method for preparing nanostructures. Due to their uniform and nearly parallel porous structures, anodic alumina membranes (AAM) have become ideal templates for the electrochemical deposition of nanowire arrays. Nanocrystalline semiconductor materials have attracted considerable attention and CdS, in particular, has been extensively studied due to its potential applications in field effect transistors (FETs), light emitting diodes (LEDs), photocatalysis and biological sensors. For electrochemical deposition of CdS nanowires, the electrolyte solution consisted of 0.055M $CdCl_2$ and 0.19M elemental sulphur in dimethyl sulphoxide (DMSO). The growth of CdS nanowires was carried out in an electrochemical cell. Surface morphology of the deposited CdS nanowires was studied using field emission scanning electron microscope (FESEM) and high resolution transmission electron microscope (HRTEM). The nanowires showed non-uniform diameters. The chemical composition of nanowires was determined using energy dispersive X-ray analysis (EDX). Experimental results showed that nanowire arrays grown in AAM behave as resonating tunneling diodes (RTDs).

Keywords*:* CdS nanowires, electrodeposition, anodic alumina membrane, resonant tunneling diode.

1. Introduction

Nanostructural materials have become attractive because of their unique characteristics. Due to the quantum confinement effect and the large surface to volume ratio, nanoparticles and nanowires show some unique physical and chemical properties. Nanocrystalline semiconductor materials such as PbS, CdS and ZnS have attracted considerable attention due to their unique properties which are missing in bulk materials (1-3). Semiconductor nanowires have been assembled into field effect transistors (FETs), p-n diodes, and light emitting diodes (LEDs), bipolar junction transistors, nanoscale lasers, gas sensors, nanoresonators and nanogenerators (4-5). CdS nanowires, in particular, have been extensively studied due to their potential applications in FETs, LEDs, photocatalysis and crossed Si-CdS nanowires recently used in nanoscale injection laser and in integrated photonics (5-8). Many novel technologies (9) have been used to prepare CdS nanowires such as the vapour-liquid-solid (VLS) process, laser assisted chemical vapour deposition (CVD), thermal CVD, metal-catalysed molecular beam epitaxy (MBE) and chemical beam epitaxy (CBE). In our investigation, we have used template-based synthesis (10-15) of CdS nanowires using anodic alumina membrane (AAM) as a template.

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It is well known that template synthesis is a simple and versatile method for preparing nanostructures within the pores of a microporous template membrane. Due to their uniform and nearly parallel porous structures, anodic alumina membranes (AAM) have become ideal templates for the electrochemical deposition of the highly anisotropic, aligned nanowire arrays. The synthesis of nanowires using AAM is one of the most attractive routes, because of its low cost, ease in fabrication and controlled growth (12). Routkevitch et al. (16) reported that *ac* electrodeposition in an AAM template is a simple and efficient method to fabricate aligned CdS nanowires. However, a density of defects such as stacking faults and twinned segments have been observed in those nanowires (17). We preferred to use *dc* electrodeposition approach to obtain aligned and well distributed nanowire arrays, as well as uniform single crystal structure.

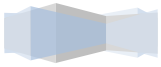
2. Materials and Methods

Commercially available AAM (Anodisc 25, Whatmann, UK) having an average pore diameter of 200 nm, a nominal thickness of 60 µm and pore density of 10^9 pores/cm^2, was used as a template. A copper film was deposited by vacuum evaporation onto the back of the template membrane.

Electrochemical cell used for fabrication of CdS nanowires has been designed in our laboratory (10). A silver rod was used as an anode and the cathode consists of copper foil attached to copper coated AAM by an adhesive tape of good conductivity.

For electrochemical deposition of CdS, we adopted the process used by Mondal *et al* (12). The electrolyte solution consisted of 0.055M $CdCl_2$ and 0.19M elemental sulphur in dimethyl sulphoxide (DMSO). This solution prevents the corrosion of AAM during the deposition. The growth of CdS nanowires was carried out for 10 min at a solution temperature of 80 ^{0}C with a *dc* potential of 2V applied between Ag anode and Cu cathode. The deposited samples were washed with hot DMSO to remove excess sulphur from the surface followed by rinsing in de-ionised water.

Surface morphology of the deposited CdS nanowires was studied using FESEM and HRTEM. For this purpose, AAM was kept immersed in 1 M NaOH for 2 hours in a beaker to dissolve alumina template. The CdS nanowires were liberated from the host matrix, washed in distilled water and dried in an oven at 50^{0}C for 30 minutes. The cleaned and dried nanowires were mounted on aluminium stubs with the help of double adhesive tape, sputtered with a layer of gold using JEOL sputter JFC 1100. Field Emission Scanning Electron Microscope (FESEM, Hitachi S-4300) was used to record cross-sectional (Fig. 1a) and lateral views (Fig. 1b) of grown nanowires at an accelerating voltage of 15 kV using different magnifications. Figure 1(b) shows the majestic view of CdS nanowires grown in a cleavage or crack along the AAM which facilitates the electrodeposition process.



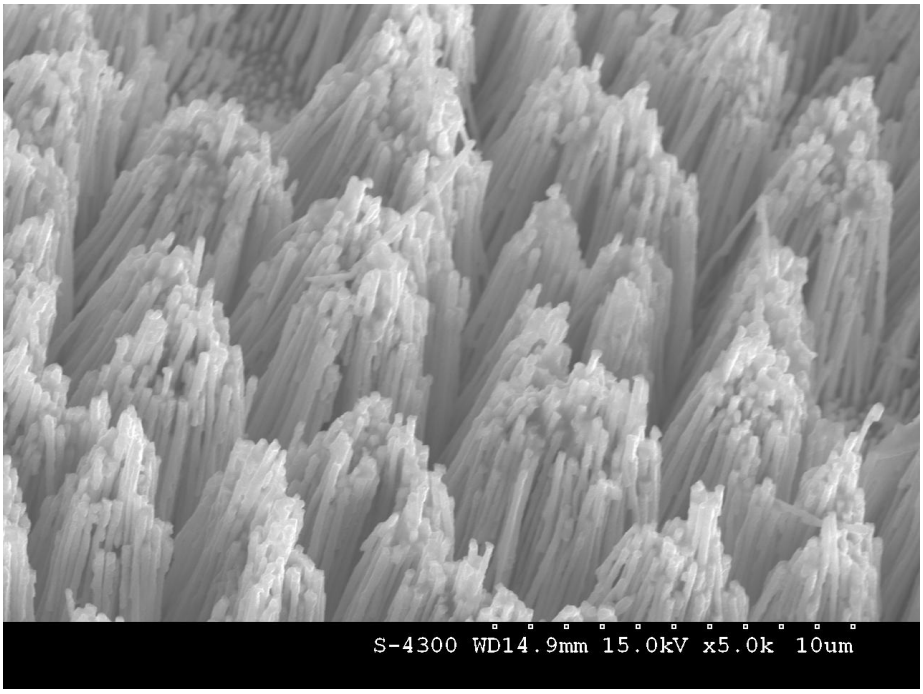


Fig. 1: (a) SEM micrograph showing top cross-sectional view of CdS nanowires

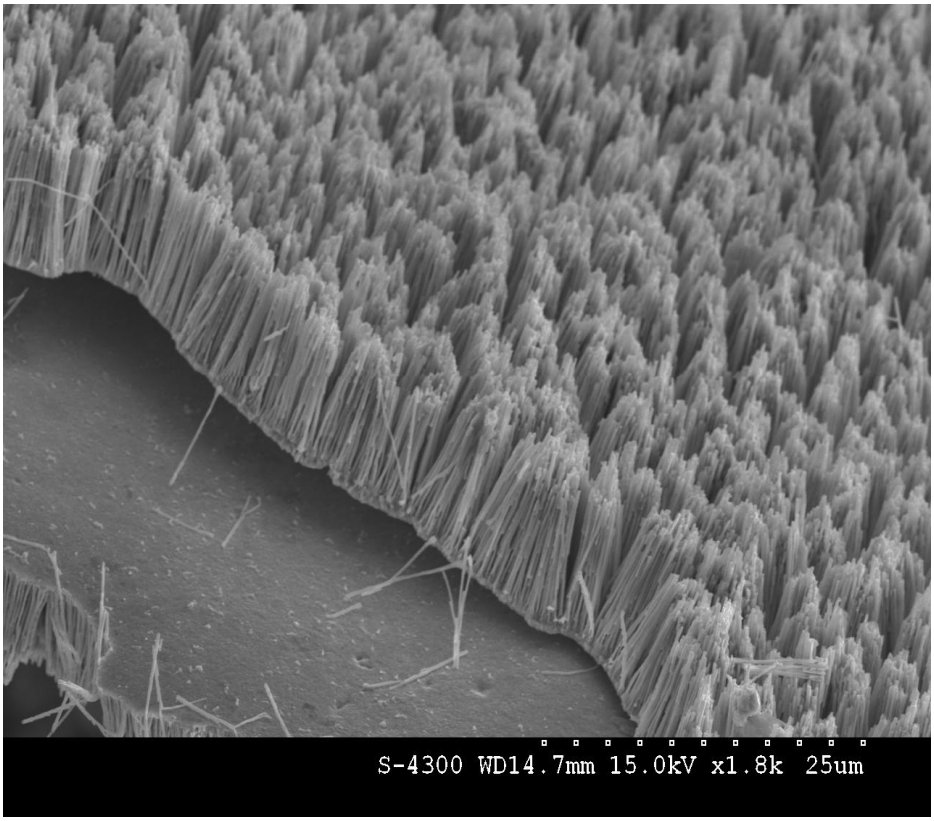


Fig. 1: (b) SEM micrograph showing lateral side view of CdS nanowires

High Resolution Transmission Electron Microscope (HRTEM, Hitachi H 7500) at Punjab University, Chandigarh was used for measurements of CdS nanowire diameters. For this purpose, nanowire arrays were removed from the template in ethanol and a few drops of this solution were loaded on carbon coated gold grids and inserted in HRTEM. Measurements were carried out in imaging mode at 80 kV under ultra high vacuum conditions as shown in figure 2 (a, b).

I-V characteristics of CdS nanowires were studied using Keithley Model 4200 SCS programmable dual source meter. Platinum probes of 0.5 µm diameter tip were used for making contacts with copper strip and nanowire arrays. I-V plot of CdS nanowires is shown in figure 3. For the quantitative compositional analysis, the chemical composition of nanowires was determined using energy dispersive X-ray analysis (EDX) technique at FESEM facility of Central Scientific Instruments Organisation (CSIO), Chandigarh.

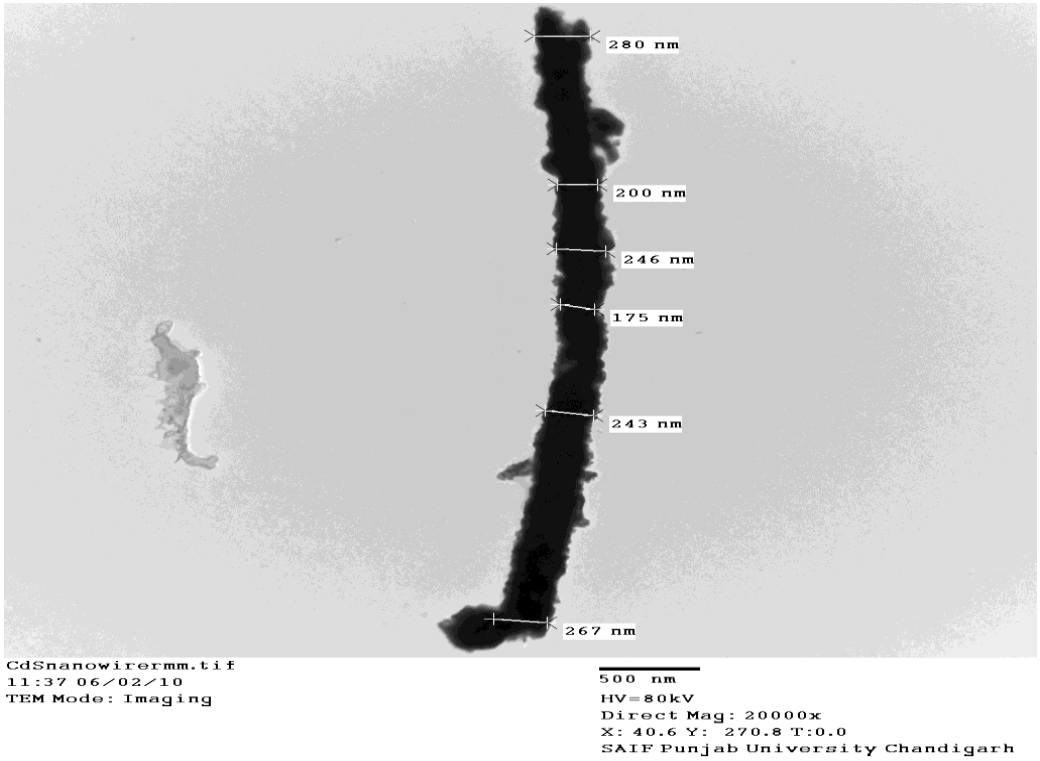


Fig. 2: (a) HRTEM image showing variation of CdS nanowire diameter

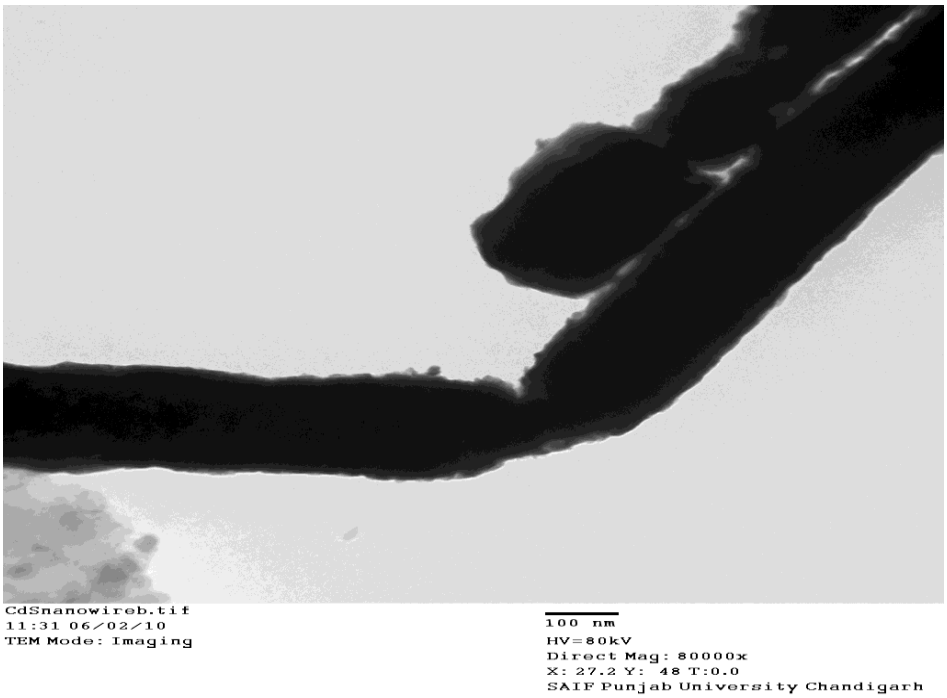


Fig. 2: (b) HRTEM image showing heterojunctions in CdS nanowires

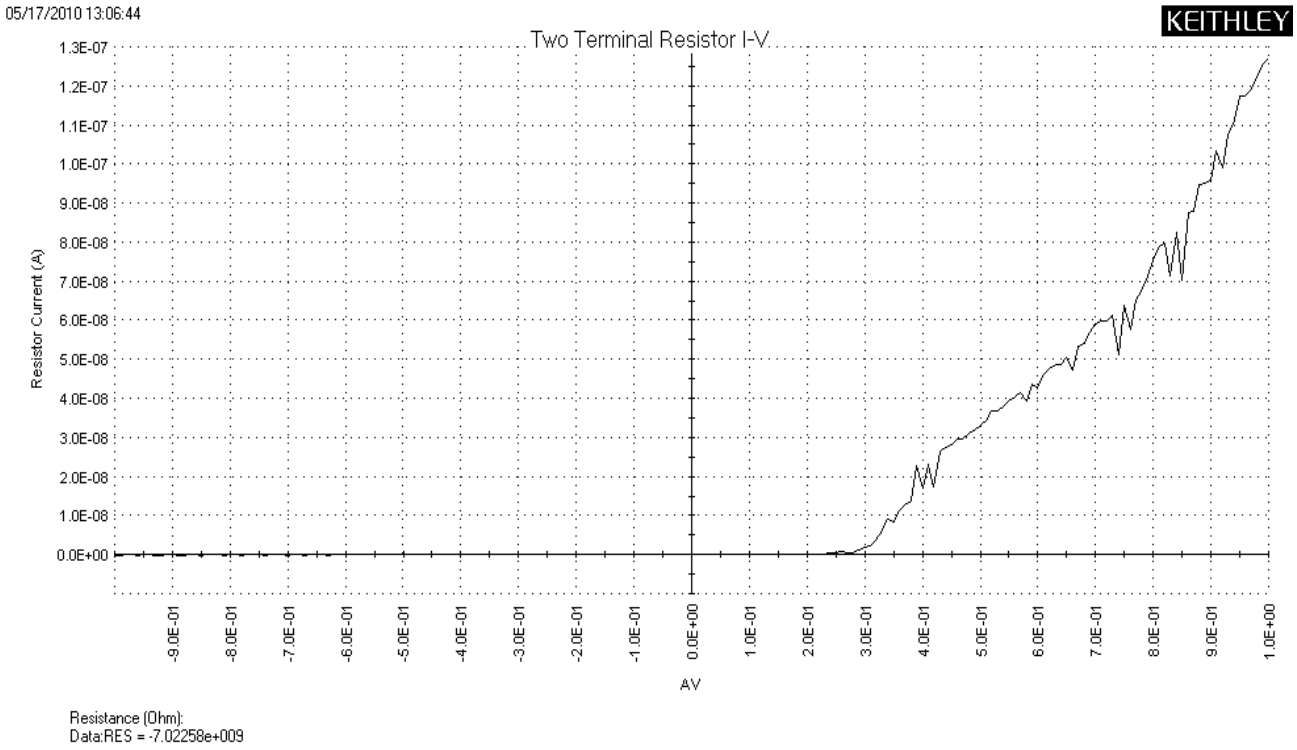
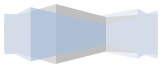


Fig. 3: I-V plot of CdS nanowire diode arrays showing RTD characteristics



3. Results and Discussion

The process for the electrodeposition (18) of CdS in the DMSO solution containing $CdCl_2$ and elemental sulphur involves three steps: First, the elemental sulphur in the solution diffuses to the electrode surface and absorbs on it. Second, the absorbed sulphur atoms undergo an electrochemical deoxidization reaction and produces S^{2-} ion. Third, the generated S^{2-} ions react with Cd^{2+} ions in the solution to form CdS crystalline core, which is fastest one among the three steps. Electrodeposition is limited to one direction in AAM pores to grow nanowires of uniform dimensions.

It is well known that nanowires offer several unique merits (4): First, nanowire devices can be assembled in a rational and predictable manner because the size, interfacial properties, and electronic properties can be precisely controlled during synthesis. Second, it is possible to have unique possibilities of building blocks not possible in conventional electronics. Third, the structure of nanowires can be rationally designed both axially and radially for creating nanodevices that exhibit both multifunctionality and integration. Our preliminary investigations establish that CdS nanowires ensembles behave as diode arrays.

Schonenberger *et al.* (19) reported that pore diameters of commercially available templates vary over a large range. The minimum to maximum diameter variation found in nanowires fabricated by them was in the ratio of 1:3. In our investigations, HRTEM micrographs show diameter variation of CdS nanowires in the range 175-280 nm (figure 2a). It clearly shows that nanowires are not perfect cylinders of 200 nm diameter but show a rugged structure from one end to the other. The aspect ratio, that is, the ratio of length to diameter, is of the order of 300. We also observed that AAM templates are very brittle and cracks appear during deposition process resulting in cleavage planes.

For the quantitative compositional analysis, the chemical composition of nanowires was determined using energy dispersive X-ray analysis (EDX) technique at FESEM facility of CSIO, Chandigarh. EDX spectrum (Fig. 4) reveals prominent peaks due to Cu, Cd and S. There are also peaks corresponding to elemental composition represented by Al, O and Cr. The Al peak is due to some residue of AAM which is not dissolved fully by NaOH treatment. The Cu peaks appear due to the effect of the substrate, which is copper film acting as the cathode. The effect of silver substrate has also been reported by Yajie et al. (20) by observing a predominant peak of silver in EDX spectrum of CdS nanowire arrays.

Table 1 represents the elemental composition of CdS nanowires. The stoichiometry of CdS is almost 1:1 by weight % composition. The atomic % composition of all the elements is summarized in Table 1. Oxygen and Copper constitute almost 50% and 25%, respectively, of total composition. Impurity peak of chromium (Cr) is not reflected in elemental composition and can be ignored. Some other authors (20-22) have reported that the atomic composition of Cd and S in CdS nanowires is close to 1:1 stoichiometry using EDX, as observed in our investigations. Sun Li et al. (22) have recently reported synthesis of sulphide nanowire arrays of CdS and ZnS through template-assisted electrodeposition. They observed phonon quantum confinement in nanowires using resonant Raman spectroscopy at room temperature.

Routkevitch et al. (16) observed that CdS nanowire arrays exhibit hexagonal CdS structure, with the crystallographic *c*-axis preferentially oriented along the length of the pore, using X-ray diffraction (XRD) and electron microscopy. Our XRD investigations (23) on CdS nanoparticles prepared by microemulsion route also revealed the hexagonal structure. Hence, we anticipated hexagonal structure for CdS nanowires fabricated in our experiment.

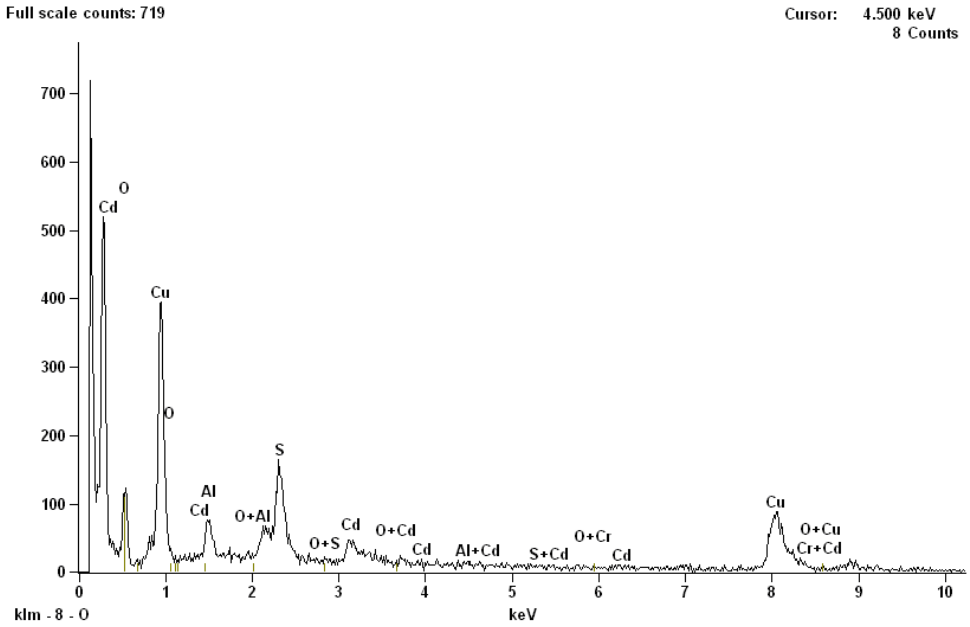


Fig. 5: EDX spectrum of CdS nanowires showing some prominent peaks

Table 1 Elemental composition of CdS nanowires

Element Line	***Weight %***	***Weight % Error***	***Atom %***	***Atom % Error***
O K	23.19	+/- 0.80	50.43	+/- 1.73
Al K	6.22	+/- 0.69	8.02	+/- 0.89
S K	11.06	+/- 0.53	12.00	+/- 0.58
Cu K	46.73	+/- 3.60	25.58	+/- 1.97
Cd L	12.80	+/- 1.94	3.96	+/- 0.60
Total	100.00		100.00	

I-V characteristics of CdS nanowires exhibit some interesting features. A prominent feature of I-V plot (Fig. 3) is a number of peaks and valleys showing decrease in current with increase of voltage, resulting in negative differential resistance (NDR). This behaviour is typical of a resonant tunneling diode (RTD) in which electrons can tunnel through some resonant states at certain energy levels. The presence of several NDR zones on the I-V plot is a definite proof of a RTD structure in CdS nanowires. HRTEM image (figure 2b) shows formation of heterojunctions of CdS. In the literature, RTDs fabricated by InAs/InP III-V nanowire heterostructures have been reported (24). It has been established that quantum size effects become pronounced as the size of the material approaches nanometer range (4).

4. Conclusions

Template synthesis using AAM is an efficient tool for fabrication of CdS nanowire diode arrays. FESEM and HRTEM micrographs reveal morphology of CdS heterostructures with non-uniform cylindrical shape. The

chemical composition and stoichiometry of CdS nanowires is dominated by the presence of Cu and O. CdS nanowire arrays exhibit RTD structure with negative differential resistance. This preliminary study opens a new route for fabrication of high performance electronic devices based on RTD behaviour of CdS nanowires.

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