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Formation of Crystalline Cadmium Selenide Nanowires

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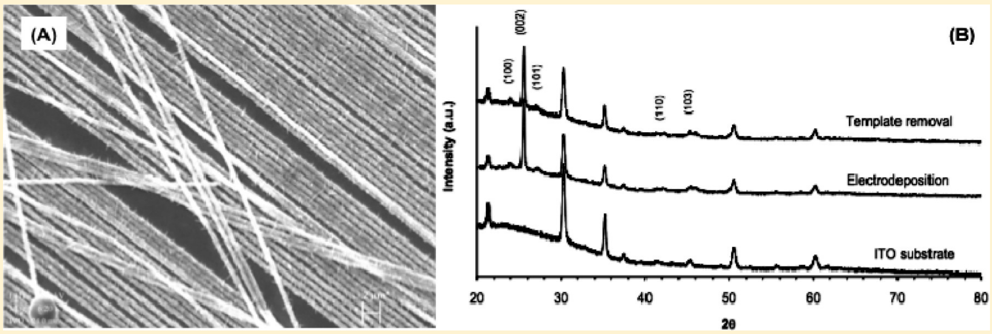
S Supporting Information

ABSTRACT:



Highly crystalline, continuous parallel arrays of CdSe nanowires have been generated through electrodeposition using photoresist templates. Easy soft imprint nanolithography (ESINL) was used to pattern a commercially available photoresist, Norland Optical Adhesive 60 (NOA 60), deposited onto the ITO substrates, prior to electrodeposition. Using the exposed ITO layer as an electrode, a thin film of CdSe was electrodeposited from an electrolyte containing $CdCl_2$, SeO_2, and HCl on the substrate, and the resist was subsequently removed in an alkaline developer solution. The resulting CdSe nanowires were 100 nm in thickness, 300−500 nm in width, and several centimeters in length. Imprinted templates were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDX). The SEM analysis confirmed the formation of parallel arrays of nanowires unaffected by the resist lift-off, and the XRD results showed that the CdSe nanowires had a hexagonal structure and that the crystalline structure was unaffected by the photoresist removal.

KEYWORDS: cadmium selenide, electrodeposition, soft nanoimprint lithography, photoresist template

INTRODUCTION

Cadmium selenide (CdSe) is an important II−VI semiconductor with a direct band gap of 1.74 eV, which is suitable for use in photovoltaic solar cells.[1,2] The control of the morphology of CdSe nanocrystals has been investigated recently after a number of studies reported the improved power conversion efficiencies of bulk heterojunction photovoltaic devices based on CdSe nanorods instead of spherical CdSe nanoparticles as the electron acceptor material.[3,4] By segregating the inorganic nanoparticle/conjugated polymer blends into vertical rods, the interfacial area between the acceptor and the donor material can be increased, providing extended pathways for holes and electrons to reach the respective electrodes, thus improving the photovoltaic cell performance.[3]

The vapor−liquid−solid (VLS) process, vapor−solid process (VS), and electrochemical deposition are the three main methods actively studied for the formation of oriented semiconductors.[2,5,6] The VLS process has largely been limited to the growth of Si or III−V semiconductors because of the need for the optimization of the catalysts. In this regard, as noted in a review by Xia et al., "one of the challenges faced by the VLS process is the selection of an appropriate catalyst that will work with the solid material to be processed into 1D Nanostructures".[6] The vapor−solid process has been mostly used to grow ZnO and Ga_2O_3 nanorods.[5] It has also been noted that a limitation of the VS process is that no tight control of the spatial arrangement has been achieved so far.[5]

Oriented semiconductors can be electrochemically synthesized within the nanopores of a porous template. Preformed porous templates are often sputtered with gold or other metals on one side of the membrane, and the semiconductors are grown electrochemically.[5−8] The pores in the template guide the formation of the semiconductors, and the orientation of the semiconductor nanorod growth is dictated by the orientation of

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the pores. The spatial control is obtained by controlling the location of the pores. This approach has been used to grow micrometer long semiconductor rods with nanometer scale diameters albeit over a small area. The template-directed synthesis has been described as a simple, high-throughput, and cost-effective procedure to create 1D nanostructures.[6] One can also use lithographic techniques to pattern an electrode array, thus gaining spatial control over a large area. The ability to work under ambient conditions, to deposit over arbitrary substrate shapes and large areas with good thickness control, and low capital cost are the key advantages electrochemical deposition provides for preparing semiconductor thin films on electrode surfaces.[9] There is growing belief that electrodeposition will become an established method in the future for semiconductor films and nanostructures synthesis.[10,11] However, to have high impact, this patterned electrodeposition needs a simple, low cost and high throughput fabrication method. This has motivated our current study.

In this current article, we address the experimental challenges and describe a new potentially low-cost and high-throughput method to generate highly crystalline, continuous CdSe semiconductor nanowires through electrodeposition using templates derived from soft nanoimprint lithography (SNIL). SNIL is the collective term for the set of nanopatterning techniques that involve pattern replication using an elastomeric mold, most notably poly(dimethylsiloxane)-based elastomers (e.g., Dow Corning Sylgard 184).[12] Our approach includes replicating a master mold in a bilayer composite daughter mold, referred to as *h*-PDMS ("hard" PDMS),[13] and imprinting onto a photocurable resist with UV irradiation at room temperature and low pressure. By using this imprinted photoresist as a template during the CdSe electrodeposition step and subsequently removing the resist (lift-off), we are able to generate continuous, uniform CdSe nanowire arrays with each wire having a thickness of 100 nm, a width of 300 nm−500 nm, and a length of several centimeters defined by the dimensions of the substrate and the mold. For electrodeposition, we have optimized the electrolyte composition and deposition potential to obtain highly crystalline, stoichiometric CdSe. Through the combination of SNIL and modified electrodeposition conditions, we report herein a straightforward and reproducible method for the stepwise fabrication of highly crystalline CdSe nanowire arrays over a large area. Our method will enable the use of continuous roll-to-roll type SNIL processes to produce CdSe nanowire arrays for a number of advanced applications. It can also be easily translated to the generation of other technologically relevant binary chalogenide nanowire arrays.

■ EXPERIMENTAL SECTION

Materials. A Sylgard 184 silicone elastomer base and curing agent were purchased from Dow Corning. Propylene glycol monomethyl ether acetate (PGMEA, ≥99.5%) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (Fluka) were obtained from Sigma-Aldrich Co. (7−8% Vinylmethylsiloxane)-(dimethylsiloxane) copolymer (trimethylsilyl terminated), (25−30% methylhydrosiloxane)-(dimethylsiloxane) copolymer (trimethylsiloxane terminated), and platinum-divinyltetramethyldisiloxane complex in xylene (2.1−2.4% Pt) were purchased from Gelest Inc. The UV-curable prepolymer, Norland Optical Adhesives 60 (NOA 60), was purchased from Norland Products Inc. All chemicals were used as received. Anhydrous cadmium chloride ($CdCl_2$, white granular powder/Certified ACS, Fisher Chemical) and selenium(IV) oxide (SeO_2, 99.8%, Acros Organics) were used as received from Fisher Scientific Inc. A Microposit MF-319 developer was purchased from Rohm and Haas Electronic Materials LLC (Marlborough, MA) and used as received. The indium tin oxide (ITO)-coated glass substrates (sheet resistance (R_s) = 8−12 Ω/square) were purchased from Delta Technologies, Ltd. (Stillwater, MN). The water used for electrodeposition studies was purified using a Millipore Milli-Q UF Plus system with a QPAK 1 column.

Characterization. Film thickness measurements were performed with a Veeco Dektak 150 profilometer. The water contact angles were measured with a VCA Optima surface analysis/goniometry system from AST Products, Inc. The reported contact angles were the average of 10 measurements of drops on different areas of the sample substrate, and the drop volume was 0.5 μL. The atomic force microscopy (AFM) images of the imprints were collected on Digital Instruments Dimension 3000 Nanoscope in tapping mode under ambient conditions using silicon cantilevers and a scan frequency of 0.702 Hz. A Trion Technology Phantom III inductively coupled plasma (ICP) reactive ion etcher (RIE) was used to etch the patterned substrates. The UV-assisted imprints were carried out using a custom built nanoimprinter fitted with an OAI 500 W UV lamp attachment (wavelength (λ) = 365 nm; intensity = 17 mW/cm^2).

X-ray diffraction (XRD) patterns of CdSe thin films were recorded using CuKα radiation (λ = 1.5406 Å) on a PANalytical X'Pert PRO diffractometer operating at 45 kV and 40 mA between 20 and 80° (2θ) at a step size of 0.016711°. The surface morphology and the structure of the CdSe nanowires were observed by scanning electron microscopy (SEM). The samples were sputtered with gold prior to SEM observation for enhanced image contrast. The SEM images were recorded using a Carl-Zeiss EVO50 series SEM at an acceleration voltage of 5−15 kV. A Bruker AXS Microanalysis energy dispersive X-ray spectrometer (EDX) was used to analyze the composition of the deposited nanowires. Transmission electron microscopy (TEM) and electron diffraction experiments of the CdSe nanowires were performed on a JEOL 2000 FX-II transmission electron microscope at 200 kV. The CdSe nanowires were floated in 1 M NaOH aqueous solution, picked up with a TEM grid, and dried overnight at room temperature.

Fabrication of the *h*-PDMS Daughter Mold. The *h*-PDMS daughter molds were prepared in a manner similar to a procedure by Odom et al.[14] Sylgard 184 silicone elastomer base and curing agent were mixed (10:1 ratio by weight) in a 100 mL dark glass bottle, covered with Al foil. The elastomer mixture was mixed for 2 min to obtain a homogeneous solution and degassed in a vacuum oven for 5 min to remove the entrapped air bubbles. The *h*-PDMS prepolymer was prepared by adding 1.7 g of (7−8% vinylmethylsiloxane)-(dimethylsiloxane) copolymer and 5 μL of a modulator (2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane) in a 20 mL vial equipped with a rubber septum and a magnetic stir bar. Nine microliters of platinum divinyltetramethyldisiloxane complex in xylene was added to the magnetically stirred mixture using a glass microsyringe. The reaction vial was placed under vacuum and backfilled with nitrogen three times. Then 0.5 mL of (25−30% methylhydrosiloxane)-(dimethylsiloxane) copolymer was added while stirring. Immediately, after the addition of the hydrosiloxane prepolymer, a polycarbonate (PC) master mold, consisting of 450 nm line spaces, was coated with a thin layer (2 μm) of *h*-PDMS mixture at 1,000 rpm for 40 s. The coated master was precured in an oven at 60 °C for 2 min. Concurrently, a thin layer of the PDMS elastomer mixture was poured in a polystyrene Petri dish. The master mold was then placed on the Petri dish, and the remaining PDMS prepolymer was dispensed onto the master of a thickness of ∼3 mm. After curing at 60 °C for 6−8 h, the *h*-PDMS replica mold was carefully peeled off from the polycarbonate master, and the edges were cut with a razor blade at the desired dimensions.

Patterning via Easy Soft Imprint Nanolithography (ESINL)[15]. The ESINL process used has been previously described in detail.[15] The 2.5 cm × 2.5 cm ITO substrates were cleaned first by rinsing with acetone and isopropanol (IPA) and then by O_2 ICP/RIE etch for 600 s under 250 mTorr pressure and at a flow rate of 49 sccm, with ICP and RIE powers of 300 and 100 W, respectively. Prior to imprinting, the *h*-PDMS mold was rinsed with methanol and tetrahydrofuran (THF) and dried under a stream of N_2 and placed on a hot plate at 60 °C to remove any residual solvent.

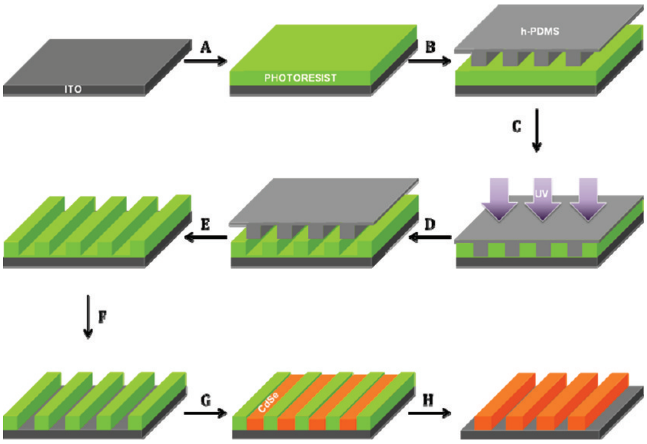

Figure 1. Schematic of the fabrication of CdSe nanowires. (A−E) Photoresist patterning via ESINL. (F) Formation of free-standing photoresist nanowires by removing the imprint residual layer via ICP/RIE O_2 plasma etch. (G) Electrodeposition of CdSe thin film on the imprinted ITO substrate. (H) Formation of free-standing CdSe nanowires after the photoresist lift-off.

A solution of NOA 60 (10 wt % in PGMEA, filtered through polytetrafluoroethylene (PTFE) membranes of pore size 0.45 μm) was spin-coated at 3000 rpm for 15 s onto the O_2 plasma-cleaned ITO substrate. The photopolymer was then exposed to UV light (λ = 365 nm) at an intensity of 17 mW/cm^2 for 15 s in air. Subsequently, the mold was placed on the precured photopolymer of 160 nm layer thickness, and the imprint was carried out at room temperature under UV in the presence of N_2 (λ = 365 nm, 17 mW/cm^2, 900 s). After the separation of the mold and the substrate, the imprint residual layer was removed by O_2 ICP/RIE etch for 17 s under 250 mTorr pressure and at a flow rate of 49 sccm, with ICP and RIE powers of 500 and 25 W, respectively.

CdSe Electrodeposition. The electrolyte solution was prepared by dissolving $CdCl_2$ (9.1 g, 49.6 mmol) and SeO_2 (0.055 g, 0.496 mmol) in 300 mL of deionized (DI) water. To this stock solution, 41.3 mL of concentrated hydrochloric acid (HCl) was added, and the solution volume was adjusted to 500 mL by adding DI water. The solution was then placed in a sonication bath for 10 min to obtain a homogeneous solution. The electrolyte had a final concentration of 0.1 M $CdCl_2$, 0.001 M SeO_2, and 1 M HCl, and a pH value of ~1.5. The electrodeposition was then carried out on the patterned ITO substrate in a three-electrode cell (cell volume = 20 mL, unstirred) controlled by a potentiostat Bioanalytical System (BAS CV-50W) voltammetric analyzer at room temperature. The cell consisted of the ITO substrate as the working electrode, Pt gauze as the counter electrode, and Ag/AgCl as the reference electrode. The films were deposited at a constant potential for 30 min. The electrochemistry used for deposition can be simply expressed as eq 1:[16]

$$H_2SeO_3 + Cd^{2+} + 6e^- + 4H^+ \rightarrow \mathbf{CdSe} + 3H_2O \qquad (1)$$

Different deposition potentials ranging from −570 mV to −610 mV resulted in the formation of hexagonal or cubic CdSe and were characterized by XRD studies.

Lift-Off Process of the Photoresist. Following electrodeposition, the samples were immersed in Microposit MF-319 developer solution under slight manual agitation. After being developed for 4 h, the substrates were rinsed with DI water and blown dry under a stream of N_2.

■ RESULTS AND DISCUSSION

The different steps of the fabrication process of CdSe nanowires are illustrated in Figure 1. *h*-PDMS molds were cast from a patterned polycarbonate (PC) master that contained features of 180 nm in height, 450 nm in width, and spaced by 350 nm. The adhesion force between the PC master and the *h*-PDMS elastomer was low, allowing good separation after curing. The water-contact angle of a freshly prepared *h*-PDMS daughter mold was measured as 113° indicating that the surface of the replica mold was fairly hydrophobic. ITO coated glass slides were used as the imprint substrates and prepared for imprinting by washing with acetone and IPA, drying under a stream of N_2, followed by O_2-plasma treatment for 10 min. The photoresist, NOA 60, was then applied to the clean ITO substrates (Figure 1A) and was precured immediately prior to imprinting by exposure to UV-radiation (λ = 365 nm, 17 mW/cm^2) for 15 s in air to improve pattern transfer. The fabricated daughter molds were durable and reusable for over 20 imprints.

Figure 2 shows the tapping mode AFM topography images and tracer profile plots of the master mold, *h*-PDMS replica mold, and imprinted and etched photoresist samples. Film thicknesses of ~160 nm were obtained by spin-coating a 10 wt % NOA 60 solution at 3000 rpm for 15 s, which was ideal for imprinting with the *h*-PDMS mold of similar pattern height. The precured photoresist was brought down toward the *h*-PDMS mold and pressed gently against it so that the photoresist would fill the gap between the template and the mold through capillary forces. The two pieces were then illuminated with an OAI 500 W UV lamp (λ = 365 nm, 17 mW/cm^2, 900 s). After the curing was completed, the two surfaces were carefully separated, and an O_2 ICP/RIE etch was used to remove the residual resist layer. Although the ICP/RIE etch was directional and biased to etch downward in thickness direction, the imprinted features were slightly etched in the lateral direction as well. All of the AFM topographic feature dimensions are summarized in Table 1.

The deposition of CdSe on patterned ITO substrates was carried out from acidic plating solution containing $CdCl_2$ and SeO_2 by applying a constant deposition potential. The deposition time and the acidity of the stock solution were systematically varied to optimize the electrochemical conditions for CdSe. The color of the ITO substrate changed from transparent to pale yellowish brown after ~5 min of electrodeposition time and to dark brown after longer electrodeposition time (≥30 min), indicating the formation of CdSe. An optimized deposition time of 30 min and concentrations of 0.1 M for $CdCl_2$, 0.001 M for SeO_2, and 1 M for HCl were selected as the standard conditions to form highly crystalline CdSe films.

Selective removal of the NOA 60 resist after electrodeposition of CdSe employed alkaline developers and was nontrivial. This required extensive experimentation to determine the optimal conditions for resist removal that would not damage the CdSe nanowire. For example, while 0.5−1 M NaOH aqueous solutions effectively removed the resist, this developer was detrimental to the electrodeposited CdSe nanowires. Scanning electron microscopy of the continuous arrays of CdSe nanowires are shown in Figure 3 with each wire having a width of ~500 nm, prepared at −590 mV and developed in 1 M NaOH solution for 1 h. While most of the CdSe nanowires remained attached to the ITO substrate after the lift-off, some nanowires were partially (Figure 3C) or completely (Figure 3D) detached from the substrate.

Further analysis of the CdSe films was carried out by using the energy dispersive X-ray spectroscopy (EDX), and the stoichiometry of the "developed" CdSe nanowires was determined. Typical EDX data are provided in Supporting Information (Figure S1 and Table S1). The elemental analysis was carried

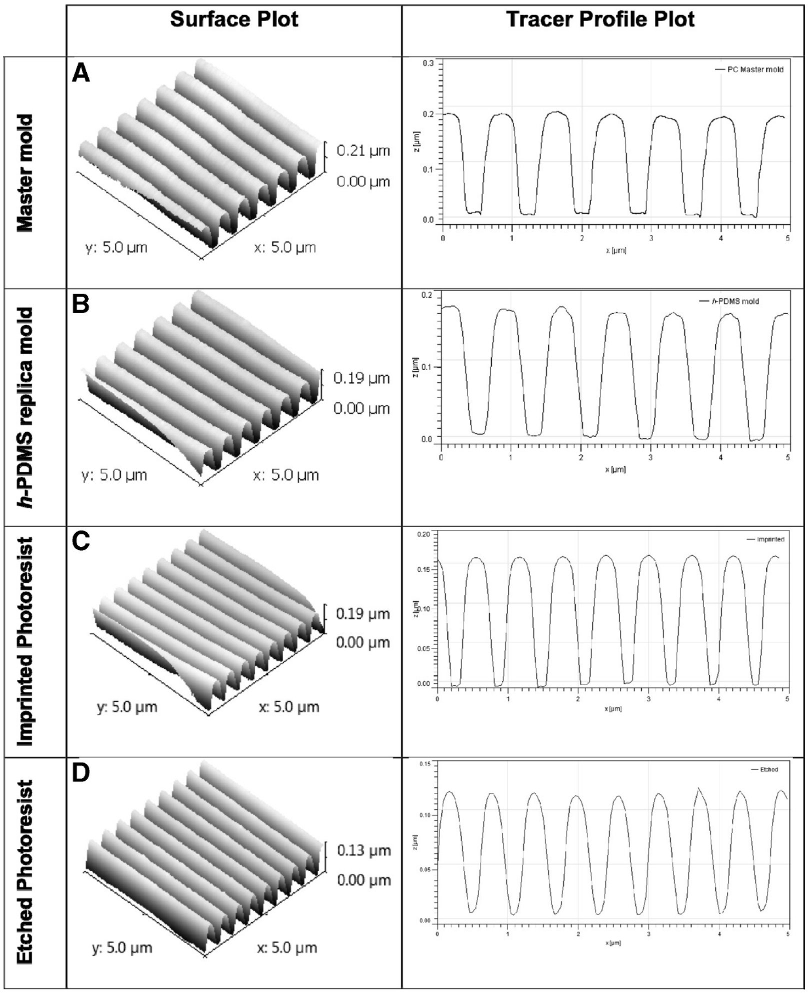

Figure 2. Three-dimensional 5 μm × 5 μm AFM topographic scans and tracer profile plots of (A) polycarbonate master mold, (B) h-PDMS daughter mold replicated from A, (C) ESINL patterned NOA 60 photoresist, and (D) free-standing photoresist imprints after the residual layer removal by O_2 ICP/RIE plasma etch.

Table 1. Topographical Dimensions of the Imprint Surfaces, as Determined by AFM

	dimensions		
sample	height (nm)	line width (nm)	periodicity (nm)
master mold	177	449	800
h-PDMS replica mold	166	439	800
imprinted NOA 60	162	370	807
etched NOA 60	110	310	807

out only for Cd and Se; the average atomic percentage of Cd:Se was 48.4:51.6 indicating that the sample was slightly selenium rich, which is in good agreement with the reports of Tomkiewicz et al.[11] and Kazacos et al.[17]

Effective removal of the resist without damaging the CdSe structures was eventually achieved by using Microposit MF-319, a tetramethylammonium hydroxide (TMAH)-based aqueous developer. The resulting CdSe nanowires were ductile, highly crystalline, and highly organized, with dimensions of 100 nm in height × 500 nm in width × 2.5 cm in length, mimicking the dimensions of the photoresist template (Figure 4A,B).

The morphology and the crystal structure of the CdSe nanowires, deposited under these standard conditions at different deposition potentials ranging from −570 mV to −610 mV, were investigated by SEM, EDX, and XRD studies.

The SEM image of the CdSe nanowires prepared at −590 mV is shown in Figure 5A. The sample was characterized by XRD before and after the photoresist removal (Figure 5B). The observed diffraction peaks at 2θ = 23.5°, 25.5°, 26.9°, 41.9°, and 45.0° corresponding to (100), (002), (101), (110), and (103) planes confirmed the formation of hexagonal CdSe crystal structure (International center for diffraction data, 01-077-0046). A detailed XRD plot is provided in Supporting Information, Figure S2. XRD analysis revealed that the crystal structure remained intact after template removal (Figure 5B).

TEM was also used to investigate the morphology and qualitatively assess the crystalline structure of the deposited crystalline CdSe nanowires. Figure 6A,B shows typical TEM image of CdSe nanowires, revealing that the nanowires are crystalline, relatively straight, and have a uniform width of ~500 nm. The highly crystalline nature of the CdSe nanowires was further confirmed by selective-area electron diffraction (SAED) as shown in Figure 6B (inset). The diffraction pattern could not be properly indexed due to the thickness of the

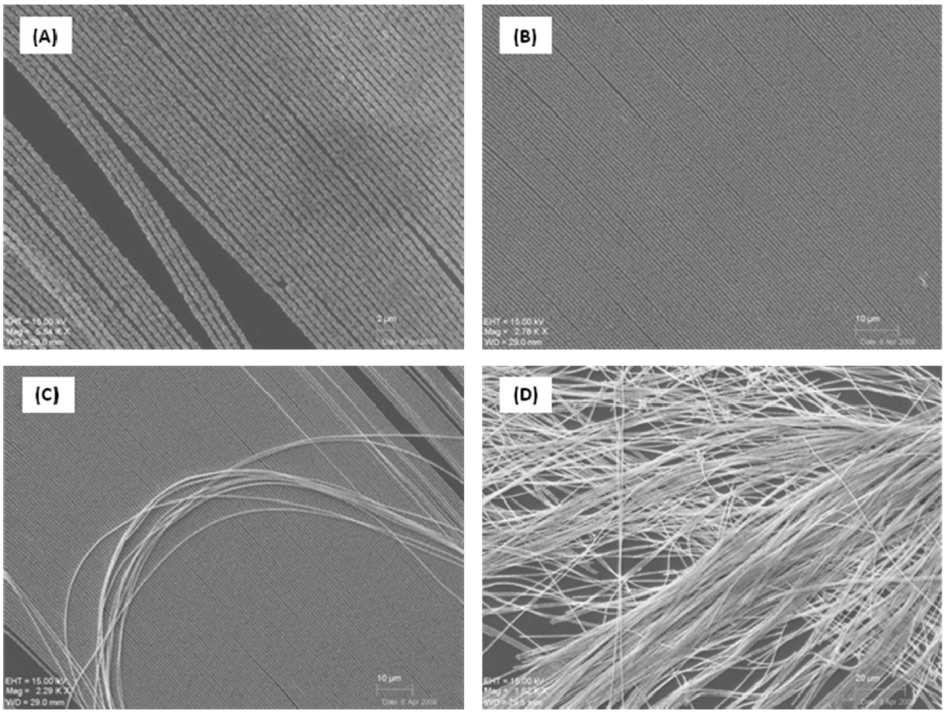

Figure 3. (A) High-magnification and (B) lower-magnification SEM images of CdSe nanowire arrays, (C) single-crystalline, and (D) polycrystalline CdSe nanowires formed by detachment from the substrate after lift-off.

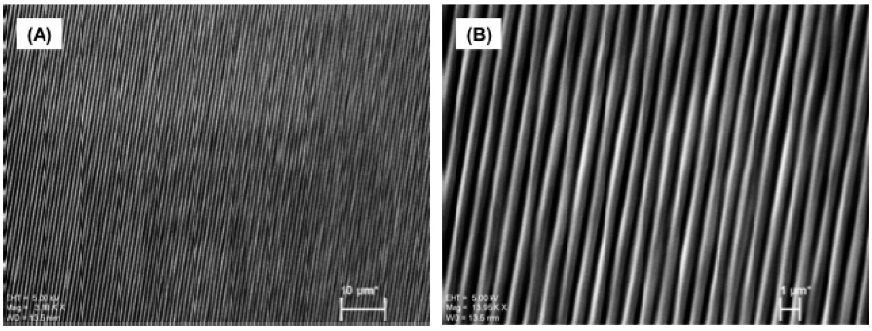

Figure 4. (A) Low-magnification and (B) higher magnification SEM images of CdSe nanowires produced at −610 mV deposition potential and developed in Microposit MF-319 solution for 4 h.

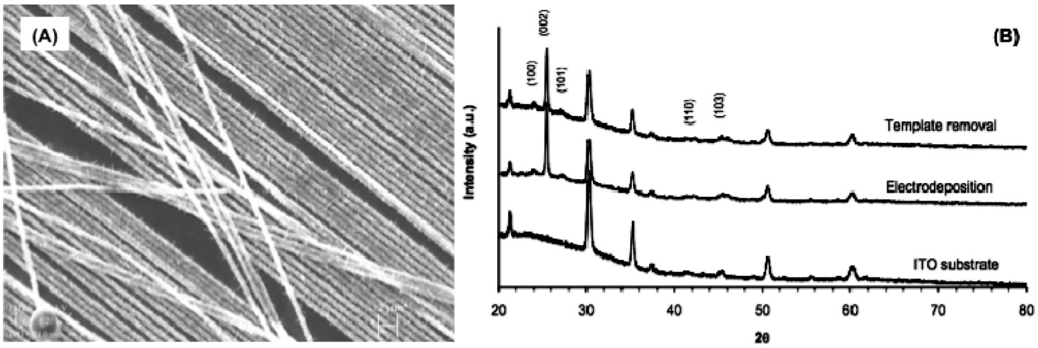

Figure 5. (A) SEM image of the CdSe nanowires electrodeposited at −590 mV and immersed in 0.5 M NaOH aqueous solution for 45 min to remove the photoresist template. (B) Aside from the diffraction peaks of the ITO substrate, peaks at 2θ = 23.5°, 25.5°, 26.9°, 41.9°, and 45.0° confirmed the hexagonal CdSe crystal structure. The crystal structure was unaffected by template removal.

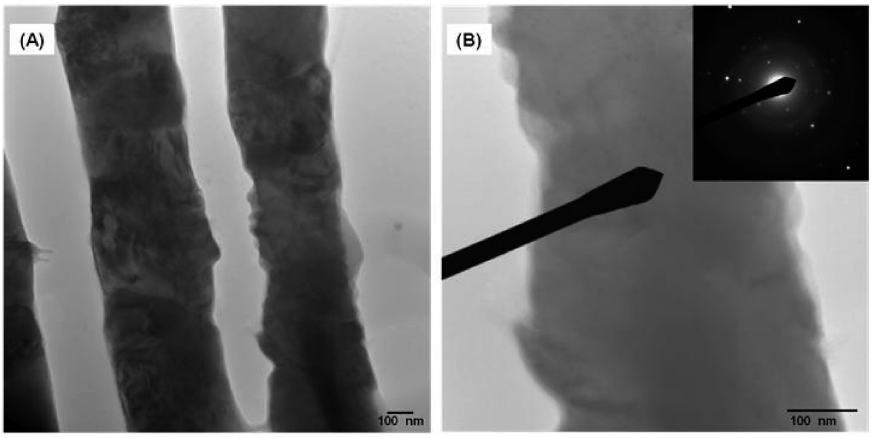

Figure 6. TEM micrographs of (A) multiple CdSe nanowires and (B) a single CdSe nanowire with a width of ∼500 nm, electrodeposited at −590 mV. SAED image (B, inset) of a single nanowire with a spotty diffraction pattern demonstrating its crystalline structure.

samples (∼100 nm); however, the clear spotty pattern indicated the crystalline nature of the nanowires.

CONCLUSIONS

In summary, we have demonstrated a novel method to fabricate continuous, crystalline CdSe nanowire arrays. We utilized a powerful new imprint lithographic pattern transfer process, ESINL, to create trenches in an imprint resist layer atop ITO-coated substrates. Subsequently, we electrodeposited CdSe from the patterned ITO surface. Lift-off pattern transfer was accomplished by optimizing the resist development process to yield free-standing crystalline CdSe wires. Additionally, we showed that the diameter and the length of the CdSe nanowires could be adjusted by controlling the parameters related to the UV-assisted ESINL imprinting process, such as mold dimensions and etching rate. XRD, TEM-SAED, and EDX analysis confirmed the formation of highly crystalline CdSe nanowires. Both SEM and TEM confirmed that the fabricated CdSe nanowires were continuous and highly uniform. We are currently using this new process to fabricate CdSe-based photovoltaic devices where our process can be used to study the effect of CdSe geometry and feature size on device performance. This and other applications will be the subject of future work.

ASSOCIATED CONTENT

Supporting Information. Additional experimental data, including energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) are provided (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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