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01 May 2015

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Growth of Ordered Nanostructure Arrays including Nanotubes and Nanorods for High Efficiency Solar Cells

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A simple and straightforward approach has been described for the fabrication of CdTe nanotube and nanorod arrays with a high degree of precision through confined electrodeposition on lithographically patterned nanoelectrodes. This technique has the potential of growing these nanotube/nanowire arrays with extreme uniformity over a significantly large area. The desired nanoelectrode pattern was defined through electron beam lithography on indium tin oxide coated glass, and electrodeposition of the semiconducting material of interest (CdTe) on the nanoelecrodes produced the nanotubes/nanowires. It is interesting to note that the measured photocurrent density of nanotube device created by this protocol exceeds that obtained from a thin film device fabricated under similar conditions by several orders of magnitude. The ability to fine tune all the physical dimensions and distribution density of the nanostructures, make this method a versatile tool to fabricate and investigate nano-structured photovoltaic devices and study their structure-property relationship. Additionally the ability to create uniform nano-feature arrays in addition to nanotube/nanorod arrays through one-step electrodeposition makes this protocol unique.

Introduction

Research and development in the field of high efficiency solar energy conversion relies heavily on the fabrication of the photo absorber materials as nanowire or nanotubular architectures, since these morphologies gives better photocurrent output with lese coverage of the active material.[1] High aspect ratio of nanostructures has an added advantage over nanoparticles and thin films since it provides appropriate thickness for light absorption while presenting an unhindered straight path for the transport of excited carriers along the length of the nanostructure.[2, 3] Moreover, in the presence of nanowires or nanorods like architectures, the efficiency achieved by a unit volume of the semiconducting material is increased by improved light absorption, light trapping and carrier collection. However, fabrication of the nanostructured semiconducting materials as vertically aligned, highly ordered nanowire or nanotubular arrays with precise distribution of size and shape over a defined location is still remains a significant technical challenge. Although there are reported methods to make ordered nanowire arrays like vapor liquid solid (VLS) growth by chemical vapor transport,[4,5] seeded growth process[6] and closed-space sublimation,[7] Most popular procedure for growing arrays of nanowires is by using hard templates like anodized aluminum,[8,9] however, it suffers from the disadvantage that this rigid template need to be removed using bases or acids to reveal the nanostructures and that process makes the semiconducting nanostructure susceptible for decomposition and hydrolysis and that can affect the photovoltaic performance of the entire device. On the other hand, shape, as well as

the physical dimensions and distribution density of nanostructures cannot be controlled as desired by this method. The simple protocol described in this report produces precise and reproducible results that provide an opportunity to explore the fabrication of ordered nanostructure arrays including nanowires and nanotubes with variable chemical compositions and a variety of nanostructure-electrode interphase to study their effect on the performance of the nanodevices. We demonstrate this concept using CdTe as the semiconducting material and indium tin oxide (ITO) coated glass as the transparent conducting substrate, where the growth of nanostructures were accomplished by electrodeposition on nanoelectrodes created on ITO coated glass substrate through electron beam lithography (EBL). By small variations of the EBL pattern definition process, arrays of nanorods, nanotubes and other interesting nanofeatures can be achieved. Electrodeposition of CdTe from aqueous solutions is a well studied technique because it is not only scalable to larger area but also a well established industrial process. Both galvanostatic and potentiostaic methods have been utilized to produce CdTe photovoltaic thin films[10] and nanorod arrays.[11, 12] In this report, the fabrication process was explained and the effectiveness of this technique was demonstrated by the enhancement in photo conversion efficiencies of the fabricated photovoltaic nanotube and nanorod arrays by using this method.

Experimental Details

Materials and Techniques. All chemicals used for preparing solutions were of analytical grade. $CdSO_4$ and TeO_2 were purchased from Sigma Aldrich and used without further purification. Polymethylmethacrylate (PMMA, mol. wt. 450K and 950K, supplied by Microchem, Newton, MA, USA) was used as the insulating e-beam resist. ITO-coated conducting glass substrates were purchased from Sigma Aldrich and had a surface resistance of 60Ω/sq. Electrodeposition was performed with IvumStat potentiostat. Powder X-ray diffraction (PXRD) patterns were taken with PANalytical's X'Pert PRO Materials Research Diffractometer (MRD, CuKα 1·5418 Å). Scanning Electron Microscope (SEM) imaging was taken using Helios NanoLab 600 equipped with energy-dispersive X-Ray spectroscopy (EDS) detector (Oxford Instruments, Abingdon, UK) for elemental analysis. EBL was performed with the in-built lithography facility available with a Helios NanoLab 600 DualBeam FIB microscope. Photoconductivity was measured through Photoelectrochemical (PEC) measurements performed with IvumStat potentiostat. A 400 W Xe lamp operating in UVA range (320–390 nm) with the intensity of 100 mW/cm^2 was used to illuminate the nanorod device.

Preparation of Samples by EBL. For the pattern definition on the ITO substrate by EBL, the e-beam resist was prepared by spin coating two layers of PMMA polymer on ITO coated conducting glass. First PMMA layer (mol. wt. 495K) was spin coated and backed for 3 minutes on a hotplate at 180°C and allowed to cool to room temperature before coating the second PMMA layer (mol. wt. 950K). Substrate was again baked for 3 minutes on a hotplate at 180°C and allowed to cool to room temperature. As prepared resist layer has a thickness about 300 nm. These PMMA layers are selectively exposed to the electron beam in the EBL process. After that the exposed area of the polymer can be removed by dipping the substrate in MIBK-IPA (1:3) solution for 55 seconds according to a reported procedure,[13] while unexposed polymer remained intact. During this pattern development process, the underlying ITO layer is exposed through the nanofeatures defined by EBL thus forming nanoelectrode islands on the substrate. During electrodeposition of the semiconducting materials on this substrate, deposition takes place exclusively on the exposed ITO through the nanofeatures while the remaining unexposed polymer acts as a soft mask inhibiting the deposition in the non-patterned areas. The experimental protocol was illustrated in Figure 1.
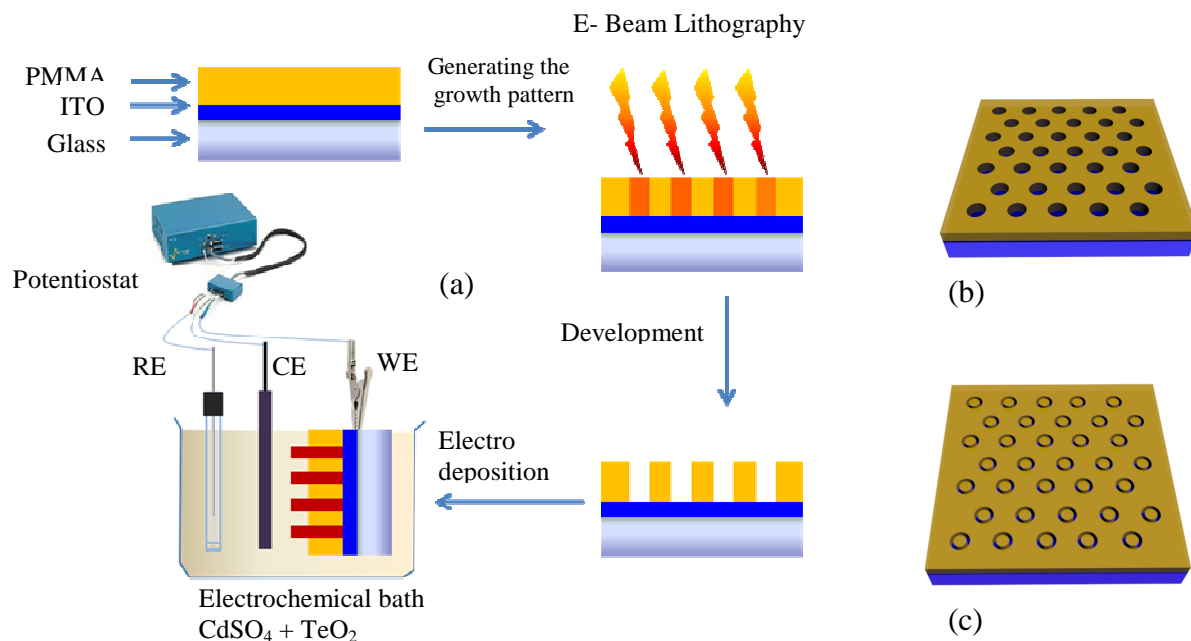
Figure 1. (a) Schematic representation of the EBL process and electrodeposition for generating CdTe nanotube and nanorod arrays on ITO coated conducting glass substrates. RE stands for reference electrode, CE stands for counter electrode and WE stands for working electrode. Representation of prepared substrate for the deposition of (b) nanorod arrays (c) nanotube arrays.

Electrodeposition of Nanotubes/Nanorods. The growth of the nanotubes and nanorods were achieved by electrodeposition on confined nanoelectrodes exposed through the EBL process. IvumStat potentiostat with standard three electrode system was used under constant potential (chronoamperometric) conditions to for the electrodeposition and an electrochemical bath containing a solution of 1.0 M $CdSO_4$ and 0·001 M TeO_2 was used according to a reported procedure for thin-film deposition of CdTe.[14,15] The deposition potential was optimum at -0.55V against Ag/AgCl reference electrode. It was seen that when the temperature was increased in the deposition bath, the crystallinity of the deposit was increased however, Te content of the deposit increases with increasing temperature. Therefore, a bath temperature of 60 – 70 ^{o}C was found to be optimum for the deposition of nanotube and nanorods. In the current process bath temperature was maintained at 65°C while the pH was adjusted to 1.8 using 1 M H_2SO_4. As prepared substrates were rinsed thoroughly after the electrodeposition with distilled water in order to remove the excess reactants from the substrate and dried under a stream of nitrogen in room temperature.

Results and Discussion

Properties of Nanotubes and Nanorods. During the electrodeposition, CdTe was deposited only on the nanoelectrodes created by the EBL process. The surrounding polymer acts as an insulating matrix preventing the deposition of the semiconducting material outside of the exposed nanoelectrodes. In addition, the growth of the nanorods or the nanotubes was guided by the polymeric nanochannel surrounding the nanoelectrode and that prevent any lateral growth of the nanorods or nanotubes thus the columnar shape of the nanotube or the nanorods remain unchanged during the growth conditions depending on the thickness of the polymer layer and the

deposition time. Rest of the polymer resist remains very clean indicating the novelty of this approach. When the electrodeposited samples were investigated in the SEM, it clearly shows the deposition has only taken place on the nanoelectrodes defined by EBL. Figure 2 shows the top view of the pattern with CdTe nanorod and nanotube arrays. The deposition of CdTe on the substrate was further confirmed by PXRD, which shows that the deposition has taken place in cubic zinc blende crystal structure.
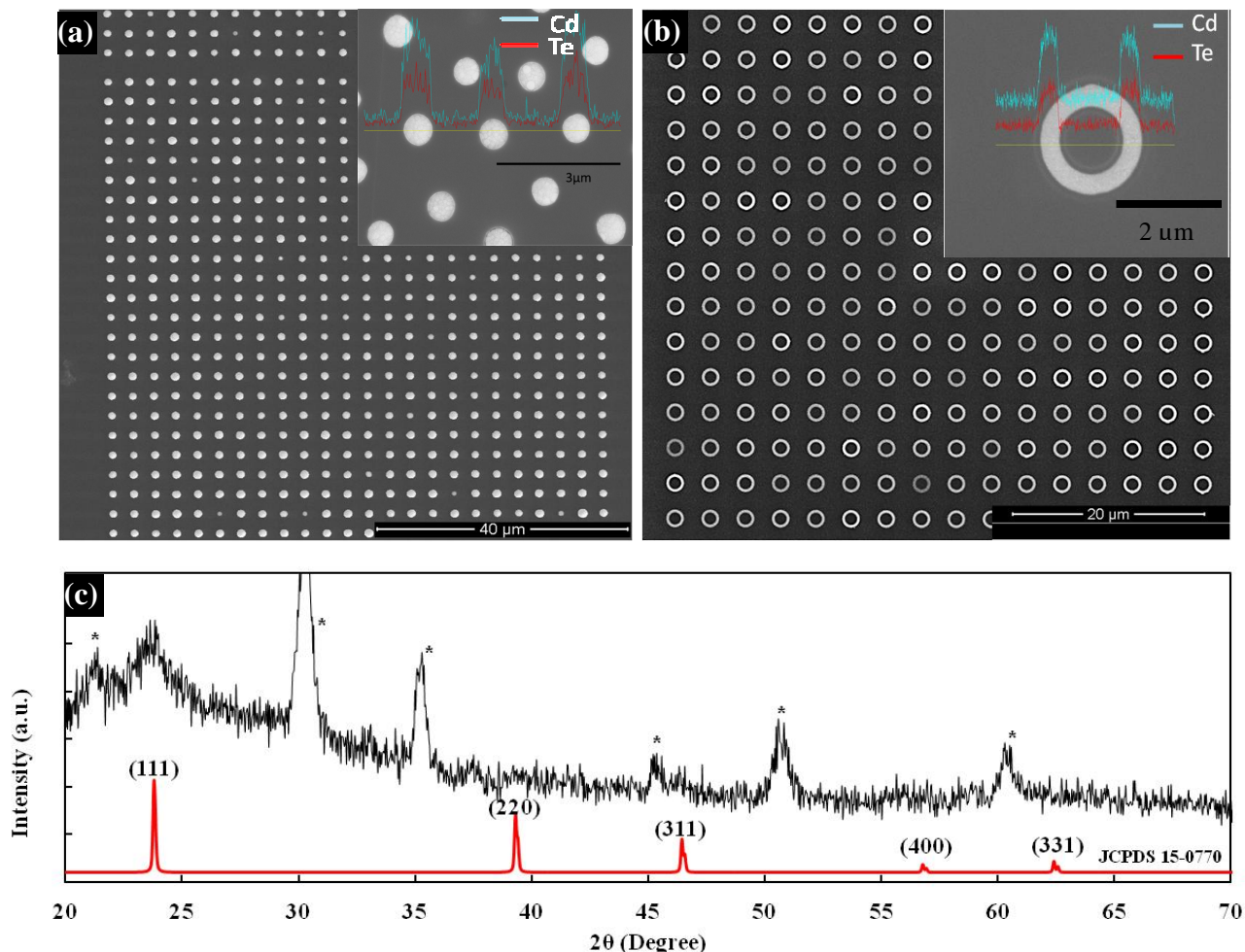

Figure 2. SEM image of CdTe (a) nanorod arrays (b) nanotube arrays fabricated by this method. Inset shows the EDX elemental line scan across the nanostructures confirming the presence of Cd and Te in the nanorods and nanotubes, respectively. (c) PXRD pattern of nanorods compared with a standard sample of CdTe. ITO peaks from the background is indicated by an asterix (*).

Considerable broadening of the (111) diffraction peak indicate that the deposition is polycrystalline with individual crystalline domains of ~39 nm as calculated from the Schrrer equation.[16] It has been reported that improved crystalline quality can be achieved if the deposition was performed at elevated temperature.[15] Same observation was made for the deposited CdTe nanostructures by this method where, weak diffraction peaks was seen for the deposition at low temperature (50 ^{o}C) while strong diffraction peaks was seen for the deposition carried out at high temperature (90 ^{o}C). However, at higher temperature deposition is very rapid and that lead to the overgrowth of nanorods and nanotubes outside of the nanochannels which alters the highly ordered nanostructure and hence deposition temperature was maintained at 65 ^{o}C. In addition, it also was seen that more tellurium tends to deposit at higher temperatures. The

pxrd pattern also shows prominent peaks of ITO which are coming from the background conducting substrate and the enhanced peak intensity of ITO mask some of the diffraction peak from CdTe.

EDX line scan was performed to confirm the elemental composition of the deposit and that shows Cd and Te on as deposited nanotubes and nanorods with 1: 1.4 ratios with slight excess of selenium which indicate the nanostructures might be p-type.[15] The length of the nanotubes or nanorods can be controlled by controlling the thickness of the polymer and also the deposition time while the diameter and wall thickness of nanotubes can be fine tuned by changing the size of the nanoelectrode defined through EBL process. As grown nanotubes and nanorods shows similar elemental composition and aspect ratio over the entire pattern. In technological point of view, this is an added advantage because the properties of the nanodevice very much depend on the size and shape of the individual functional nanostructures.

Enhanced Photoelectrochemical (PEC) Response. Generation of the photocurrent was monitored by photoelectrochemical response measurements of the nanotube and nanorod arrays according to a reported procedure.[17] Three electrode system containing the substrate with nanorod arrays as the working electrode, Ag/AgCl reference electrode and Pt counter electrode was used in a buffer solution of 0.1 M acetic acid, 0.1 M sodium acetate and 0.1 M sodium sulfite and having a pH of 4.6 as the electrolyte medium. The device was illuminated with a 400W Xe lamp operating in UVA range (320–390 nm) with the intensity of 100 mW/cm^2. To monitor the difference between photocurrent and the dark current the light source was chopped at regular intervals to provide a light on-off environment. Figure 3 shows a comparison of generated photo current from the nanodevices and a thin film device fabricated under similar conditions.
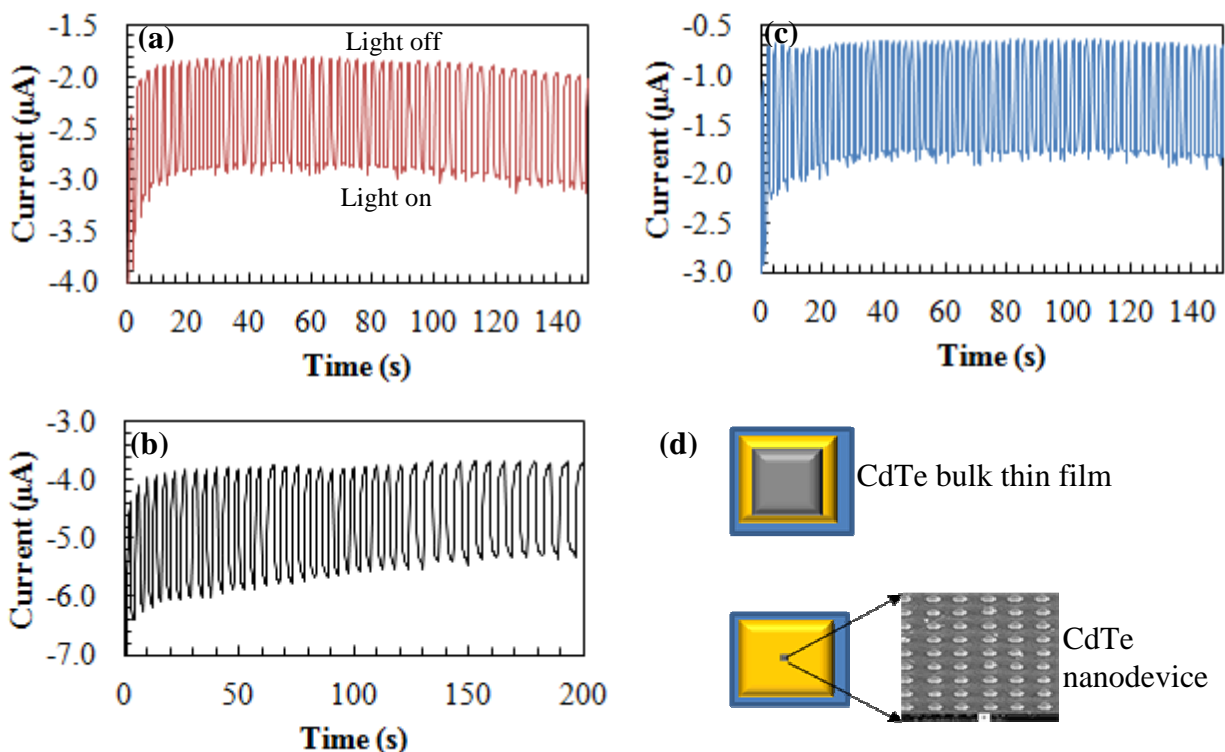

Figure 3. Generated photocurrent at an applied bias of -0.4 V from the (a) nanotube device (b) nanorod device and (c) thin film device under similar testing conditions. (d) shows a graphical

comparison of the area from which the photocurrent was generated. Total area covered by the photoactive material of nanodevice is about 12% compared to the coverage of the thin film.

Same measurements were carried out on a thin film of CdTe grown on ITO substrate under similar electrodeposition parameters to obtain a comparison of photocurrent with the nanodevice. As a controlled experiment, PMMA coated ITO substrate (blank sample) was also used for the measurement of the photocurrent to demonstrate that blank sample generate no noticeable photocurrent under these experimental conditions. The negative photocurrents obtained from the devices indicate that the deposited CdTe is p-type conductivity. It was noted that CdTe nanorod arrays showed a photocurrent density more than twice of that obtained from the thin film device besides the actual coverage of the active material in the nanorod device is much smaller (12%) compared to the thin film device. PEC measurements of the nanotube array device shows that a similar photocurrent to the nanorod device can be achieved with even less area of total coverage compared to the nanorod device. Nanotube arrays will especially be useful for photo conversion due to the larger available surface area compared to nanorod arrays, which can improve photocurrent generation per unit volume of the semiconducting material. The above observation confirms that having larger surface area of nanotubes delivers better efficiency than nanorods per unit volume. However, fabricating such vertically aligned nanotube arrays are very challenging and reports of CdTe or other semiconducting nanotube arrays are very limited. The fabrication of nanotube arrays described in this protocol is a novel concept and it is independent of the material need to be deposited or the conducting substrate. Typically any type of semiconducting material can be electrodeposited on a given conducting substrate using this protocol. The novelty of this method can be appreciated by looking at the cleanliness of the deposit, uniformity of the nanotube diameter and the wall thickness throughout the entire pattern as it was seen in Figure 2(b). These patterns can be generated over a larger area through a sequential EBL process.

Enhanced photocurrent can be attributed to several factors. If the nanorods or nanotubes are below the ray optics limit, significant light absorption can be achieved by resonance light trapping,[1] which can generate a higher photocurrent. Three dimensional geometry of the vertically aligned architecture can also direct to a reduced optical reflection leading to enhanced photo absorption.[18] For thicker nanorods or nanotubes it can be considered as each nanorod or nanotube acts as a resister and the current output from a parallel series of resisters can be enhanced according to the Ohm's law. Hence, for vertically aligned thicker nanorod or nanotube arrays current can be amplified even though the photo absorption is not significantly enhanced. The physical dimensions of the CdTe nanorod and nanotube arrays are slightly larger than the threshold limit for resonance light trapping and therefore, most probably the enhancement of the photocurrent is due to the parallel arrangement of the nanostructures in a small space and a higher volume of the photoabsorber. Simulated results predict that further reduction of nanofeature size will lead to electromagnetic resonance in the nanorods and nanotubes. This will enhance photo absorbance and can potentially amplify the photocurrent generation. Authors are currently trying to fabricate thinner nanorod, nanotube and other types of nanostructure arrays with even smaller pitch and study the effect on the generation of the photocurrent.

Conclusion

We have successfully developed a protocol to fabricate ordered nanostructure arrays including nanotubes and nanorods by electrodeposition on lithographically patterned nanoelectrodes. As fabricated nanorod and nanotube arrays shows highly uniform physical dimensions and elemental composition. The photocurrent generate from the nanorod device is comparable to that of thin film device even though the coverage of the active material in the nanorod device is a

fraction of the thin film device. Nanotube device produces a similar current with even lower coverage than that of the nanorod device thereby indicating the potential of this method to fabricate high efficiency nanodevices. This protocol provide an opportunity to study the effect of the morphology to the photo absorption and photocurrent generation through fine tuning of each physical dimensions such as diameter of nanorod and nanotubes, nanotube wall thickness, the distance between adjacent nanotube or nanorods, packing density of the arrays and shape. The other advantage of this process is that these ordered arrays can be fabricated on any conducting substrate including flexible substrates. Since electrodeposition was employed for the growth of nanorod and nanotube arrays, complex structures like tandem solar cells can be easily achieved through sequential electrodeposition of the material of interest where morphology control is extremely challenging.

Acknowledgments

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