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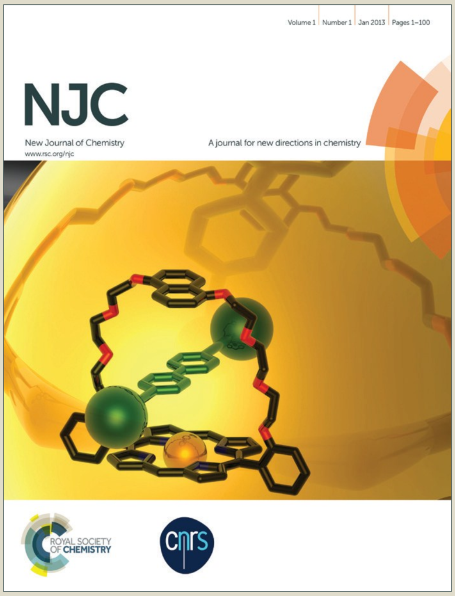

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In-situ growth of CdTe nanostructures from novel electrodeposition bath: Tuning of electrical properties and reuse of ionic liquid†

Khushbu R Chauhan,[a] Dipal B Patel,[a] and Indrajit Mukhopadhyay *[a]

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We report a one-pot, surfactant free and catalyst free electrochemical synthesis of CdTe spindle like nanostructures directly on the substrate from a single ionic liquid electrolytic bath. The growth mechanism of CdTe nanostructures is revealed by investigating the structural growth in different deposition time domains. The physical dimensions of CdTe nanostructures were varied by changing Te:Cd ratio in the bath, maintaining 1:1 stoichiometry of Te:Cd in the growing thin film. Maintaining the stoichiometry is necessary for its use in the solar photovoltaic devices. A simple configuration Cu:FTO:p-CdTe:Cu was utilized to study the impact of CdTe structures on the electrical properties of the diode. The I-V measurements and admittance spectroscopy revealed that the electrical properties of the diode improve systematically by increasing the diameter and length of the CdTe nanostructures. We also show an efficient reuse and optimized use of the ionic liquid for the electrodeposition of CdTe nanostructures.

1 Introduction

The semiconducting nanostructures are of great use in the field of electronics due to their tunable properties. The electronic properties of such nanostructures can be greatly altered by changing their physical dimensions[1]. The modification of semiconducting nanoparticles into 1D, 2D and 3D superstructures is necessary to extract some extraordinary properties. Many groups have successfully manipulated the dimensions of semiconducting material and claimed a drastic change in their electronic[2], optoelectronic[3,4] and optical[1,5] properties compared to the bulk material. However, it is very difficult to control the physical characteristics of the nanostructures and the successful synthesis indeed always needs an in depth knowledge of the growth mechanism. Nanoparticle assemblies of two different materials into a binary superstructure with a precise control over its composition is a challenging task[6,7]. Various techniques like template assisted method[8,9], electrochemical method[10,11]and self-assembly of particles[12] have been adopted by researchers for obtaining metal or semiconducting nanostructures. Electrochemical route has proved to be an efficient tool for the synthesis of nano-microstructures by various means. A well-known template assisted electrochemical growth of nanostructures has opened up a whole new field of accurately fabricating either metal or semiconductor structures directly on the substrate[13–16]. Being simple, cost effective and versatile technique, electrochemical deposition has gained a great acceptance from researchers. However, all the reports on the electrochemical route are based on the aqueous or non-aqueous solutions[17,18] where a direct growth of nanostructures is not possible. Since discovery, in-spite of having extraordinary properties, the use of ionic liquids (ILs) is confined to the reactive metal electrodeposition[19–21] and merely for the semiconductor electrodeposition[22–25]. Although the aqueous and non-aqueous solutions provide a satisfactory synthesis of thin films[26–28], their use is limited up to a certain temperature and potential window. On the contrary, ILs can be used at elevated temperatures and large voltages to deposit the thin films having desired properties[29]. There are variety of ILs[30,31] having suitable properties for the electrodeposition of electronic or solar grade semiconducting thin films. A few reports are found on the use of IL for the synthesis of nanostructures[32–36] but no report claimed till date on the synthesis of nanostructured CdTe thin film from IL medium. Since years, CdTe is being used in X-ray or gamma-ray detectors, solar cells and photodiodes[1,37–39]. Researchers[40–44] have successfully deposited highly crystalline CdTe nanostructures from aqueous media, but very few reports[45] deal with one to one correspondence of structure-electronic properties. In our initial studies we have showed a successful fabrication of CdTe nanostructures from BMIm Cl bath[38], however in depth study of growth mechanism and tuning of the structures were challenging tasks. One of the concerns with the use of ionic liquid for the electrodeposition process is the lack of efficient recycling techniques.

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[a] *School of Solar Energy, Pandit Deendayal Petroleum University, Raisan, Gandhinagar-382007, India Fax: +91-79-23275030; Tel: +91-79-23275303; E-mail: indrajit.m@sse.pdpu.ac.in*

Chrobok[46,47] showed the recycling process of IL in which he recovered 89 % ionic liquid after recycling and the recycled ionic liquid was used for at-least three times.

In this paper, we demonstrate a one pot synthesis of CdTe spindle like structure network over the transparent conducting oxide glass(F:SnO_2,FTO) substrate direct from IL bath. The growth mechanism is established and the key affecting parameters for the synthesis of stoichiometric and different sizes of nanostructures are discussed. A direct correlation between physical and electrical properties of the structures is shown when the junction between substrate and nanostructured CdTe film acted as a Schottky rectifier. We have also showed a way out for the optimized use of the ionic liquid, in particular BMIm Cl, for the electrodeposition of CdTe nanostructures.

2 Experimental

The precursors for the electrodeposition of nanostructured CdTe thin films were anhydrous cadmium chloride (99.99 % pure, Aldrich) and tellurium dioxide (99.9% pure, Aldrich). The IL, 1-butyl-3-methylimidazolium-chloride ($\geq$ 98% pure, water $<$0.2%,Bromide $\leq$ 25 mg/kg, Phosphate$\leq$ 30 mg/kg,Aldrich) was used as solvent, mediator and catalyst for the direct synthesis of nanostructured CdTe thin film on F:SnO_2 (resistivity 15 Ω/square, 2.2 mm thickness, Aldrich) substrate. A four stage cleaning with trichloroethylene, alcohol, acetone and double distilled water was done to thoroughly clean any residue from the substrates. A Potentiostat/Galvanostat (Autolab) was used to supply a constant potential necessary for the electrodeposition of stoichiometric CdTe film[48]. A platinum wire was used as a quasi-reversible reference electrode and platinum wire (area 115 mm^2) was used as a counter electrode. The resultant films were characterized by X-Ray Diffractometer (XRD, X'pert PRO, PANalytical), Scanning Electron Microscope (SEM, Ultra-55, Zeiss), Energy Dispersive X-ray (EDX, Inca,Oxford), Transmission Electron Microscope (TEM, JEOL, JEM 2100), UV-Vis (Shimadzu-2600), conductance (PGSTAT302N, Autolab) and I-V (U2722A, Agilent) measurements for its physical, optical and electrical properties.

3 Results and Discussion

3.1 Proposed Growth Mechanism of CdTe nanostructures

In order to thoroughly understand the in situ growth of the nanostructures, an electrolytic bath containing Te and Cd precursors in the molar ratio of 1:40 in 3 mL BMIm Cl was used for the deposition of CdTe thin films on F:SnO_2 substrates for different deposition time. The potential necessary for the deposition of stoichiometric CdTe was identified on the basis of number of independent experiments and observations[48]. It is worth to note here that the conventional route of acidic aqueous medium for the electrodeposition of CdTe thin films never lead to the growth of nanostructures directly on substrate.

The FE-SEM images showing coverage of the substrate after different time of deposition are given in Figure-1. We have studied the I-t transients of the individual components of CdTe alloy, i.e. Cd and Te[49]. It was confirmed by the analysis of I-t transients that electrodeposition of this binary compound from the ionic liquid medium progresses as consecutive nucleation and growth of Te and Cd clusters. We also found from EDX analysis that after 2 second of electrodeposition, only Te nuclei covers the FTO substrate via forming a channel network (Fig.1(a)). It is known that the metal ions of Te exists as $TeCl_6$ anions in ionic liquid[50] and the formation of such complexes brings the reduction potential of Te and Cd ions closer to eachother for the co-deposition. The applied potential of -1.45 V vs Pt is well above the standard reduction potential of Te^{4+} species[48] and hence the growth of Te clusters starts before the whole substrate gets covered by Te monolayer. It was observed that channel growth of Te cluster continues till 20 second of deposition time as shown in Fig.1(b). This predeposited Te layer acts as a seed layer for the nucleation of Cd and Te-Cd chain starts forming after 40 second of deposition time (as evidenced by EDX). As Te clusters are forming rather than a Te monolayer, number of available Te sites (nanoclusters) for the nucleation of Cd increases. It can be seen from Fig. 1(d) that interconnected Te-Cd deposits cover the whole substrate after 2 minutes of deposition. As deposition prolonged for 5 minutes, a compact layer of well-connected CdTe nanostructures was obtained. At this point of time, we obtained only Te rich film and hence the deposition was continued further. Electrodeposition for longer duration (10 minutes, Fig 1(f))leads to an overgrowth of CdTe one dimensional nanostructures and stoichiometric composition is reached till the deposition time of 17 minutes. We believe that the formation of CdTe nanostrucures should follow the following reaction mechanisms.

$$TeCl_6^{2-} + 4e^- \rightarrow Te + 6Cl^- \tag{1}$$

$$Cd^{2+} + 2e^- + Te \rightarrow CdTe \tag{2}$$

The co induced deposition is well explained by kroger[51] who stated that the deposition potential of compound is determined by the electronegative component, i.e. Te in present case. The similar phenomenon of co deposition is also considered for the electrodeposition of PbTe from ionic liquid medium[52]. A schematic to represent the growth of CdTe nano spindles is shown in Figure-2 and the variation in CdTe stoichiometry with time is shown in Figure-3.

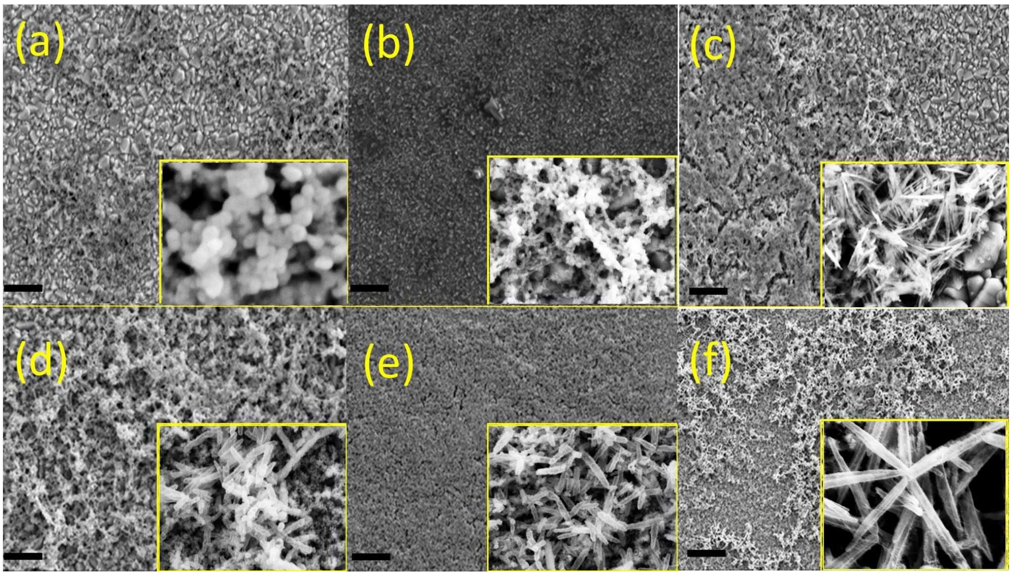

Fig. 1 FE-SEM images showing the substrate coverage after (a) 2 second (b) 20 second (c) 40 second (d) 2 minute (e) 5 minute (f) 10 minute, scale bar shows 2 μm length and inset shows the magnified (at 75K X) images of deposited area.

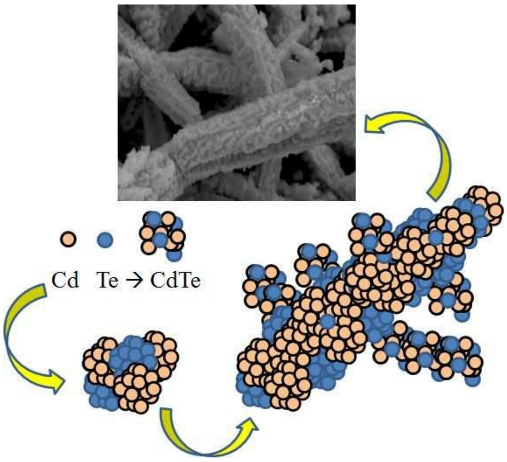

Fig. 2 A schematic showing the growth of CdTe nanostructures.

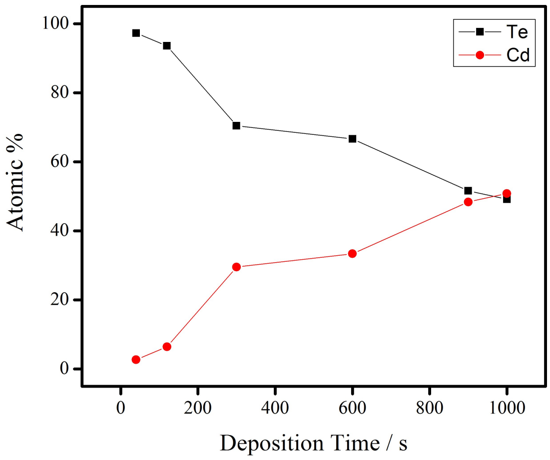

Fig. 3 Variation in stoichiometry of CdTe film with deposition time.

3.2 Film Properties

The XRD pattern of the deposited CdTe nanostructured film is shown in Figure-4. The structures possess a preferred orientation along (220) plane of the cubic CdTe, with small traces along (111), (222) and (200) planes.

The HRTEM image and electronic diffraction pattern of the structures is shown in Figure-5. The inter-planner spacing calculated from the images came out to be 0.34 nm which corresponds to the (200) and (111) planes of the cubic CdTe, confirming the results obtained from XRD data. The spot diffraction pattern confirms the high crystallinity of the deposited CdTe structures. The EDX spectrum of the deposited nanostructured film is shown in SI-Figure-1. The EDX results confirmed that the overall film as well as individual structures is of 1:1 stoichiometry of CdTe. The optical absorbance, transmittance and reflectance measurements were carried out to find the band gap of the deposited thin film. The Tauc plot confirmed a direct optical band gap of 1.5 eV (shown in SI-Figure-2) for all the films.

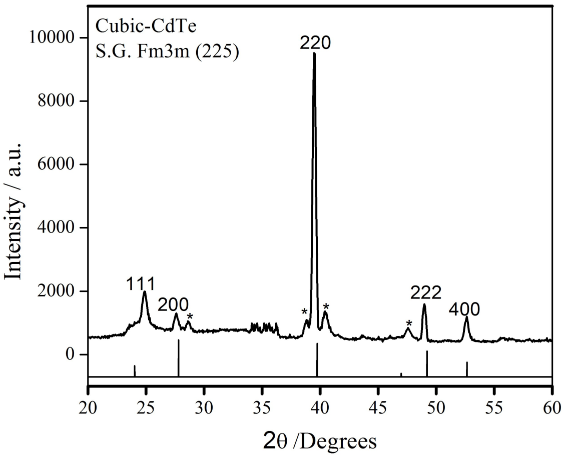

Fig. 4 XRD spectrum of the deposited nanostructured CdTe thin film compared with standard database for cubic CdTe, where * represents the FTO peaks.

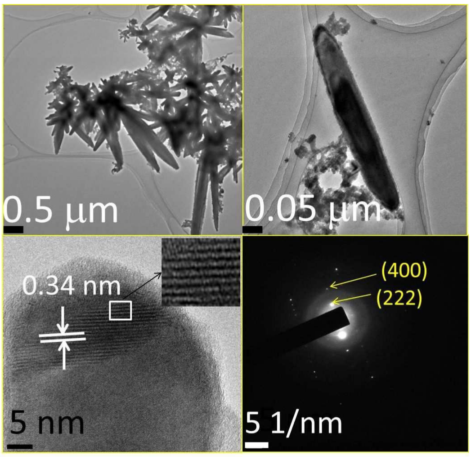

Fig. 5 TEM analysis of the CdTe nanostructures.

3.3 A direct Correlation between Structure-Electrical properties

3.3.1 Tuning of CdTe nanostructures As we showed in our preliminary studies that the potential to deposit CdTe in perfect stoichiometry is only -1.45 V vs. Platinum quasi reversible electrode, the variation in applied potential was not a possible way to tune the dimensions of the structures in order to maintain its required composition. However many studies claim the dependency of dimensions of structures on the applied potentials[39] where stoichiometry is not a concern. We have also tried to vary the deposition temperature from 80 to 110 °C for possible change in the structural properties; however the increase in temperature increased the growth rate of such structures, hardly changing any dimensions. Hence the only possible way to tune the dimensions of CdTe nanostructures was to vary the precursor concentration in the bath. It is worth to note here that for the electrodeposition of stable electronic or solar grade CdTe thin film, it is necessary to supply much more Cd^{2+} ions in the bath[17,18]. In order to keep this criteria and yet to change the physical dimensions of the structures, the Te:Cd molar ratio was varied as 1:10, 1:20 and 1:40. As it can be seen from Figure-6, the variation in molar ratio of the precursors leads to a successful tuning of the dimensions of nanostructures. Going from minimum to maximum allowed Cd concentration in the bath under identical experimental conditions, both the diameter and length of the CdTe nanostructures increased linearly. The average length and diameter profile of the structures is given in SI-Figure-3. In our previous work, we showed a great enhancement in the rectification property of CdTe nanostructures compared to a granular CdTe thin film[38]. In order to see the effect of nanostructures on the electrical properties of the diode, the I-V measurements were carried out. All the diode parameters obtained from the assessment by standard diode theory are discussed in the next section.

3.3.2 I-V Measurements All the films based on CdTe nanostructures having different dimensions were configured as Cu:FTO:p-CdTe:Cu Schottky diodes to see the effect of nanostructured CdTe on the junction properties. The I-V characteristic of the different films is compared in the Figure-7. A systematic enhancement in the diode properties is noticed as the dimensions of the structures increase. According to the diode fabrication and the arrangement of CdTe nanostructures over the substrate, it would be more scientific to correlate the electrical properties with both the diameter and length.

All the electrical parameters of the diodes based on CdTe nanostructures with different dimensions are listed in Table-1. It can be seen from the table that by increasing the dimensions of the nanostructures, the rectification ratio increased as 16, 162 and 5800, respectively. Such experimental evidences have been presented for Schottky diodes made with CNT[53]. The one dimensional CdTe Nano-spindles are having good conductivity compared to CdTe granules and hence favor optimal charge flow due to presence of relatively less grain boundaries. The rectification ratio also depends on the series resistance of the diode and conductance of the active material. It was observed that by increasing the dimensions of the CdTe nanostructures, the conductance of the diode increases drastically. It was also noticed that by increasing the size of structures, the series resistance of the diode decreases in several orders. This is because, as the diameter of the structure increases, the carriers are free to move in the material without colliding with

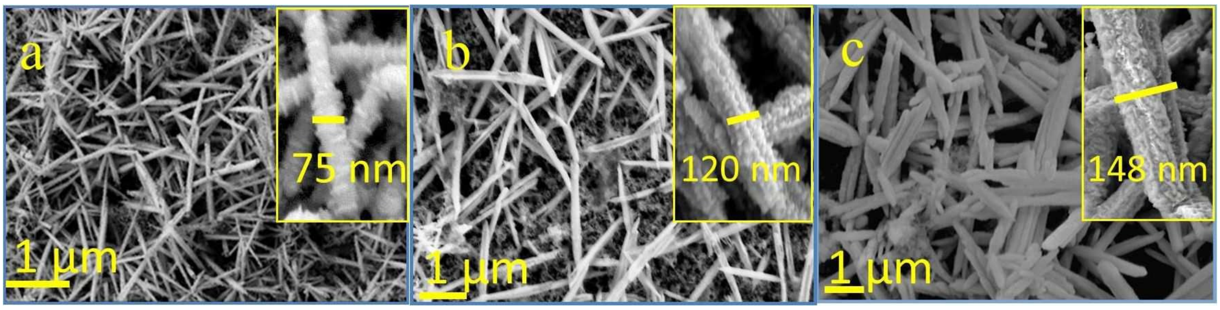

Fig. 6 Variation in length and diameter of the structures with change in precursor concentration Te:Cd as (a) 1:10 (b) 1:20 (c) 1:40

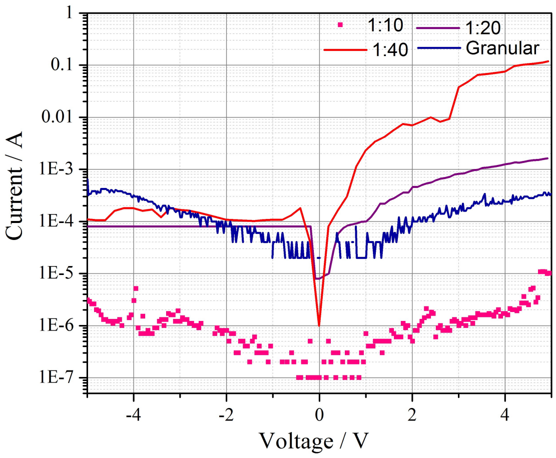

Fig. 7 I-V characteristics of CdTe granular and films deposited via different molar concentration of Te:Cd in IL bath.

each other. The improvement in the breakdown region of the diode is found optimum for the structures with highest dimensions. This can be understood by assuming CdTe granules as shunting sites in the diode and hence the films with more CdTe granules than the CdTe nanostructures make a poor schottky junction with the substrate. However, the source of leakage current is still not found for many nanostructure systems due to lack of experimental support[54].

3.3.3 Two Probe Admittance Analysis The admittance measurements were done for two purposes. Firstly to quantify the conductance of diodes with structures of different dimensions and secondly to study the junction properties. As discussed in above section, the conductance of diode increases by changing the dimensions of CdTe structures. Our arrangement of Cu:FTO:p-CdTe:Cu makes the simplest possible way to accurately measure the conductance from CdTe nanostructures and electrical properties of the diode. In order to examine the effect of CdTe structures on the device properties, identical diodes based on CdTe nanostructures having different dimensions were studied. The diode admittance was recorded as a function of applied frequency in the range of 0.7 MHz to 7 Hz. As recorded admittance spectra for the films with different dimensions of CdTe structures are shown in Figure-8. Admittance spectra itself revealed the reason for the high performance of highest dimension (length and diameter) structures. The corresponding electrical equivalent circuit shown in the inset of Figure-8 was used for further analysis. In the circuit, R_s is the series resistance (independent of bias), G_s is the conductance and C_j is the capacitance of the diode. It was found that the granular film results in to the series RC equivalent circuit of the diode with a little change in its capacitance with bias. However for a Schottky rectifier, one expects a parallel combination of bias dependent R and C. Hence the diode with the granular CdTe behaves as a soft Schottky diode, which conducts almost the same amount of current in reverse and forward bias conditions. Whereas, the nanostructured CdTe thin film makes nearly ideal Schottky junction with the sub-

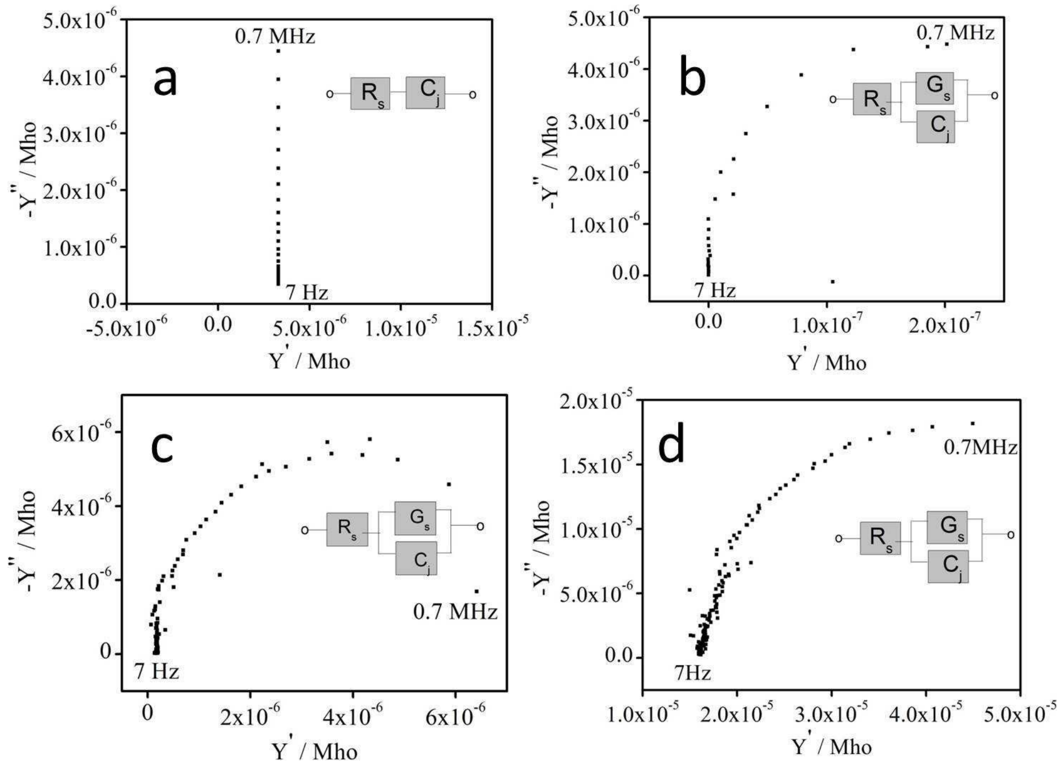

Fig. 8 Admittance spectra of (a) Granular CdTe thin film (b) D = 75 nm, L = 1.2μm (c) D = 120 nm, L = 1.8μm (d) D = 148 nm, L = 2.7μm

strate FTO and operates only in forward bias conditions. It can be also seen from Table-1 that the value of capacitance is minimum for the diode with highest dimensions structures and maximum for the granular CdTe thin film. This claims that CdTe granules act as a capacitive load during the diode operation. Hence it is expected that the diode with the CdTe granules will allow a large reverse current because of partial removal of the minority carriers which results in high switching time. The films with the CdTe nanostructures also comprise of CdTe granules and hence allow more reverse current than only a nanostructure will allow. Thus one can assign CdTe granules as a source of leakage in the diode operation. The values of room temperature conductance for CdTe structures are listed in Table-1. A systematic increase in the conductance of the diode is related to the increase in the dimensions of the structures. The value of conductance of the highest dimensions structures is comparable with the CdTe thin film deposited by vacuum based technique[55]. The increase in conductance with the increase in dimensions leads to drastic change in their electrical properties as Schottky rectifiers.

3.4 Efficient reuse of ionic liquid BMIm Cl for Electrodeposition of CdTe thin film

We have showed in our previous study that a constant potential of -1.45 V (vs. Platinum quasi reversible reference) is necessary for the electrodeposition of adherent, smooth and stoichiometric CdTe thin film. The charge-time profile confirmed the thickness of 2 μm after deposition time of 3600 seconds[48]. For re-using the same ionic liquid bath for the deposition of almost identical CdTe thin films, one has to control its deposition conditions. For simplicity, we assumed 100% Faradic efficiency of the deposition process, and hence each time the same amount of precursors were added in the ionic liquid bath so that Te:Cd as 1:40 is maintained. Since all other parameters were optimized, only the thickness control was a tricky task. The charge transfer profile for each deposition cycle is shown in Figure-9. It was confirmed by number of experiments, that the time required for the same amount of charge to be transferred is less when the same ionic liquid is used for 2nd to 4th cycle. This may be understood as, the ionic liquid used in the first cycle with the precursors of cadmium and tellurium generates complexes in the bath and these complexes facilitate the growth of Te nuclei for the second cycle of deposition. We have also noticed that the viscosity of ionic liquid changes significantly after each cycle of

Table 1 The parameters for CdTe nanostructures derived from D.C. and A.C.analysis

Avg. diameter (D) nm	Avg. length (L) μm	Series Resistance (from DC analysis) Ω	Rectification Ratio @ 5V	Conductance @ 0.5 V and 0.7 MHz Siemens	Capacitance @ 0 V and 100 Hz F
Grains	-	1.01×10^4	102	4.09×10^{-6}	5.38×10^{-10}
75	1.2	1.85×10^4	16	1.93×10^{-7}	1.8×10^{-10}
120	1.8	1.78×10^3	162	3.36×10^{-6}	2.55×10^{-11}
148	2.7	3.00×10^2	5800	1.09×10^{-5}	8.9×10^{-12}

deposition. However, detailed analysis of this observation is beyond the scope of this study. The increased growth rate after first deposition cycle might be due to a significant change in the viscosity of the ionic liquid, which again facilitate the charge transfer process. To have the same thickness of the film after each deposition cycle, the charge-time profile was continuously monitored. As the identical charge transfer during the first cycle is achieved, the electrodeposition process was stopped. It can be seen from the charge-time profile that from third cycle onwards less than half of the time is required to achieve same thickness. The same procedure of adding an equal amount precursors and monitoring the charge transfer was applied for at-least four cycles. After each deposition cycle we observed noticeable change in the color of ionic liquid (photographs shown in SI-Figure-4). To understand such process, we took TEM image of the used ionic liquid dispersed in methanol. The TEM images of the samples after each reuse is shown in SI-Figure-5. It was confirmed from the TEM images that the ionic liquid itself stabilizes some nuclei after first deposition run. Such nuclei can act as seeds to grow CdTe structures for the second deposition cycle and hence decreases the deposition time as compared to the first run. When the reuse of ionic liquid reaches at 5th cycle, the ionic liquid contains much more cadmium precursor than the required amount for the stoichiometric CdTe electrodeposition. Hence the reuse of ionic liquid BMIm Cl without any purification was limited up to four cycles to electrodeposit stoichiometric CdTe thin films of identical characteristics.

4 Conclusions

In conclusion, high quality CdTe nanostructures were directly synthesised on the F:SnO$_2$ substrate to obtain thin film from a single ionic liquid electrolytic bath. The deposition parameters were varied in such a way that 1:1 stoichiometry of Cd:Te is maintained. The dimensions of the nanostructures were tuned for its optimized performance as an active layer of Schottky diode. The admittance spectroscopy revealed that the conductance of the diode changes from 1.93×10^{-7} to 1.09×10^{-5} Siemens by increasing the length and diameter of the CdTe nanostructures. We have showed a way to reuse the ionic liquid bath up to four times to obtain CdTe nanostructured thin film. The current investigation provides a new route to get thin film based on CdTe nanostructures, the dimension of which can be varied to obtain interesting electronic and opto-electronic properties.

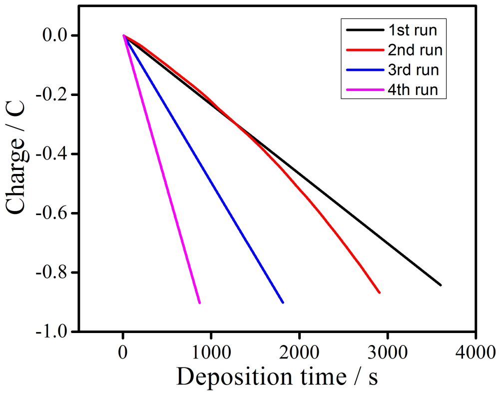

Fig. 9 Profile of time required for same charge transfer for successive deposition runs using same ionic liquid bath with added precursors.

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References

1 Y. Ye, L. Dai, T. Sun, L. P. You, R. Zhu, Y. J. Gao, R. M. Peng, D. P. Yu and G. G. Qin, *Journal of Applied Physics*, 2010, **108**, 044301–4.
2 B. Hu, L. Mai, W. Chen and F. Yang, *ACS Nano*, 2009, **3**, 478–482.

3 N. C. Greenham, X. G. Peng and A. Alivisatos, *Phys. Rev. B*, 1996, **54**, 17628–17637.

4 D. B. Patel and I.Mukhopadhyay, *International journal of advanced research in science and technology*, 2014, **3(1)**, 44–50.

5 C. B. Murray, D. J. Norris and M. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706–8715.

6 S. Sun, X. Zhang, J. Zhang, X. Song and Z. Yang, *Cryst. Growth Des.*, 2012, **12**, 2411–2418.

7 E. V. Shevchenko, D. Talapin, N. Kotov, S. O'Brien and C. Murray, *Nature Letters*, 2006, **439**, 55–59.

8 D. Bera, S. C. Kuiry, S. Patil and S. Seal, *Applied Physics Letters*, 2003, **82**, 3089–3091.

9 R. Al-Salman and F. Endres, *J. Mater. Chem.*, 2009, **19**, 7228–7231.

10 F. Favier, E. C. Walter, M. P. Zach, T. Benter and R. M. Penner, *Science*, 2001, **293**, 2227–2231.

11 O. Hofft and F. Endres, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13472–13478.

12 Q. Zhou, B. Wang, P. Wang, C. Dellago, Y. Wang and Y. Fang, *CrystEngComm*, 2013, **15**, 5114–5118.

13 M. Zach, K. Ng and R.M.Penner, *Science*, 2000, **290**, 2120–2123.

14 T.Ishizaki, N. Saito and O.Takai, *J.Electrochem.Soc.*, 2009, **156**, D413–D417.

15 D. Wang, W. Zhou, B. McCaughy, J. Hampsey, X. Ji, Y.-B. Jiang, H. Xu, J. Tang, R. Schmehl, C. OConnor, C. Brinker and Y. Lu, *Advanced Materials*, 2003, **15**, 130–133.

16 T.Ohgai, L. Gravier, X. Hoffer and J.-P. Ansermet, *J. Appl. Electrochem.*, 2005, **35**, 479–485.

17 M. H. Milesed and W. S. McEwan, *J. Electrochem. Soc*, 1972, **119**, 1188–1190.

18 J. Llabres, *J. Electrochem. Soc.*, 1984, **131**, 464–465.

19 A.P.Abbott, C. Eardley, N. Farley, G. Griffith and A.Pratt, *J. Appl. Electrochem.*, 2001, **31**, 1345–1350.

20 S.Z.E.Abedin, E. Moustafa, R. Hempelmann, H. Natter and F.Endres, *Electrochem. Commun.*, 2005, **7**, 1111–1116.

21 J.-Y. Zhang and W. W. Yu, *Applied Physics Letters*, 2006, **89**, 123108–3.

22 M. K. Carpenter and M. W. Verbrugge, *J. Mater. Res.*, 1994, **9**, 2584–2591.

23 M. C. Lin, P. Y. Chen and I. W. Sun, *J. Electrochem.Soc.*, 2001, **148**, 653–658.

24 F. Endres and S. Abedin, *Chem. Commun.*, 2002, **20**, 892–893.

25 M. H. Yang, M. C. Yang and I. W. Sun, *J. Electrochem. Soc.*, 2003, **150**, 544–548.

26 W. J. Danaher and L. E. Lyons, *Aust. J. Chem.*, 1984, **37**, 689–701.

27 K. Uosaki, M. Takahashi and H. Kita, *Electrochim. Acta*, 1984, **29**, 279–281.

28 C. Sella, P. Boncorp and J. Vedel, *J. Electrochem. Soc.*, 1986, **133**, 2043–2047.

29 M. Armand, F. Endres, D. MacFarlane, H. Ohno and B. Scrosati, *Nature Materials*, 2009, **8**, 621–629.

30 S.Hatrik and P.Zahradnik, *J. Chem. Inf.Comput.Sci.*, 1996, **36(5)**, 992–995.

31 K. M.Docherty and C. KulpaJr, *Green Chemistry*, 2005, **7**, 185–189.

32 R. Al-Salman, X. Meng, J. Zhao, Y. Li, U. Kynast, L. M. M. and F. Endres, *Pure Appl. Chem.*, 2010, **82(8)**, 1673–1689.

33 J. Ma, J. Lian, X. Duan, Z. Liu, P. Peng, X. Liu, T. Kim and W. Zheng, *CrystEngComm*, 2011, **13**, 2774–2778.

34 C. Vollmer and C. Janiak, *Coordination Chemistry Reviews*, 2011, **255**, 2039–2057.

35 P. Migowski, G. Machado, S. R. Texeira, M. C. M. Alves, J. Morais, A. Traverse and J. Dupont, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4814–4821.

36 M. Scariot, D. O. Silva, J. D. Scholten, G. Machado, S. Teixeira, M. Novak, G. Ebeling and J. Dupont, *Angewandte Chemie International Edition*, 2008, **47**, 9075–9078.

37 A. M. Smith and S. Nie, *Journal of American Chemical Society*, 2011, **133**, 24–26.

38 K. R.Chauhan and I. Mukhopadhyay, *J. Appl. Phys.*, 2014, **115**, 224506–7.

39 M. C. Kum, B. Y. Yoo, Y. Rheem, K. Bozhilov, W. Chen, A. Mulchandani and N. V. Myung, *Nanotechnology*, 2008, **19**, 325711–325718.

40 J. Lei and H. Ju, *Chem. Soc. Rev.*, 2012, **41**, 2122–2134.

41 Z. Deng, O. Schulz, S. Lin, B. Ding, X. Liu, X. Wei, R. Ros, H. Yan and Y. Liu, *Journal of American Chemical Society*, 2010, **132**, 5592–5593.

42 H. Zhang, D. Wang, B. Yang and H. Mohwald, *Journal of American Chemical Society*, 2006, **128**, 10171–10180.

43 M. Saruyama, M. Kanehara and T. Teranishi, *Journal of American Chemical Society*, 2010, **132**, 3280–3282.

44 S. Banerjee and S. S. Wong, *Journal of American Chemical Society*, 2003, **125**, 10342–10350.

45 A. M. Smith, A. M. Mohs and S. Nie, *Nature Nanochnology*, 2009, **4**, 56–63.

46 A.Chrobok, *Tetrahedron*, 2010, **66**, 2940–2943.

47 A.Chrobok, *Tetrahedron*, 2010, **66**, 6212–6216.

48 K.R.Chauhan, I. Burgess, G. Chang and I.Mukhopadhyay, *J. Electroanal. Chem.*, 2014, **713**, 70–76.

49 K. R.Chauhan, D. B. Patel and I. Mukhopadhyay, *Electrochim. Acta*, Under Review.

50 F.Golgovici, A. Cojocaru, M. Nedelcu and T.Visan, *Chalcogenide Letters*, 2009, **6**, 323–333.

51 F.A.Kroger, *J. Electrochem. Soc.*, 1978, **125(4)**, 566–572.

52 F.Golgovici and T.Visan, *Chalcogenide Letters*, 2011, **8(8)**, 487–497.

53 H. M. Manohara, E. W. Wong, E. Schlecht, B. D. Hunt and P. H. Siegel, *Nano Letters*, 2005, **5(7)**, 1469–1474.

54 A. Zabet-Khosousi and A.-A. Dhirani, *Chem. Rev.*, 2008, **108**, 4072–4124.

55 G. Rusu and M. Rusu, *Solid State Communications*, 2000, **116**, 363 – 368.