IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 10, Issue 4 Ver. I (Jul. – Aug. 2018), 07-14
www.iosrjournals.org

Effect of Annealing Temperature on the CdSe/FTO (SnO_2:F) Nanowires Grown by Chemical Bath Deposition

Hulya Metin Gubur[1,2*], Fethiye Septekin[1], Soner Alpdogan[2], Sevda Ildan Ozmen[1]

[1]*Advanced TechnologyResearch& Application Center, Mersin University, TR-33343Yenisehir, Mersin, Turkey.*
[2]*Department of Physics, Mersin University, TR-33343, Yenisehir, Mersin, Turkey*
**Corresponding author: HulyaMetinGubur*

Abstract:*The Cadmium Selenide (CdSe) nanowire thin films were grown on FTO substrates by chemical bath deposition (CBD) at 70 °C and annealed in an air atmosphere at a different temperature. Corn-like nanowire structure was observed when the CdSe/FTO nanowire thin films were annealed at 573, 673 and 773 K. It was determined by scanning electron microscope (SEM) that the diameters of the CdSe/FTO nanowires and corn-like nanowires were around 20–40 nm. X-ray diffraction (XRD) results showed that these films had a mixed phase of cubic and hexagonal. It was observed that the energy band gap decreased from 1.84 eV to 1.53 eV as a result of the shifting of the absorption edge of the annealed films towards low energy with increasing annealing temperature. The resistivity measurements of the all films were made by using four-probe methods. It was seen that the resistivity of the films decreased with the increasing temperature. The conductivity of the nanowire and corn-like nanowire films annealed at 573 K, 673 K and 773 K were found to be the best.*

Keywords: *CdSe/FTO, corn-like nanowires, thin films,four-point probe method*

Date of Submission: 23-06-2018 Date of acceptance: 05-07-2018

I. Introduction

One-dimensional (1-D) nanostructures such as nanotubes, nanobelts,nanowires and nanorods have been studied extensively in the past few decades because of their exclusive optical, mechanical,thermal, electronic and magnetic properties [1, 2, 3]. These one-dimensional structures are being used as parts in the fabrication of electronic, optoelectronic, electrochemical and electromechanical devices and the connection of these units [4]. Among the 1-D nanostructures, semiconductor nanowires have been the subject of intensive research [5] for their potential use in the nanoscale applications such as light generation, light detection sensing and photovoltaics [6, 7]. Especially II-VI binary semiconducting compounds have been extensively investigated due to their unique optoelectronic properties [8, 9, 10, 11].

CdSe thin film which belongs to the II-VI groups semiconductors, has attracted intensive attention because of the direct band gap (1,73 eV), high absorption coefficient and tunable band gap changing from infrared to ultraviolet area for the applications in solar cells, thin film transistors, photodetectors,light emitting diodes, biomedical imaging devices, gas sensors and other optoelectronic devices [12, 13, 14, 15, 16, 17, 18, 19]. Electronic and optical properties of CdSe thin films are sensitive to the deposition conditions and technique that are used [11, 15]. The nanowires that are made of the CdSe semiconductor material absorb sunlight and generate power. Until now, tapered CdSe nanowires or CdSe grain structures have been prepared with various techniques such as CBD, electrodeposition, molecular beam epitaxy, spray pyrolysis, thermal evaporation. Among all of these methods, CBD is a low-cost technique and simple for deposition on large areas [21-24].

In this study, the CdSe nanowire thin films with 0.7 µm thickness were grown on FTO substrates by the CBD method at 70 ºC. The films were annealed in air atmosphere. The structural, optical and electrical properties of the as-deposited and annealed CdSe/FTO nanowire thin films were characterized by XRD, SEM, energy dispersive X-ray (EDX) and four probe techniques.

II. Experimental contents and measurements

The CdSe nanowire thin films were deposited on FTO substrates byCBD at 70 °C which contained chemical solutions with 12.5 g sodium sulfite, 0.225 M sodium selenosulfate, 1 M cadmium nitrate, 1 M TEA, % 25 ammonia solution, and double-deionized water. More details including the substrate cleaning and the deposition method were explained in our previous publication [23]. The CdSe nanowire thin films were fabricated as six films and were annealed in air atmosphere at temperatures from 373 to 773 K. Finally, the structural, optical and electrical properties of thin films were characterized by the XRD, SEM, EDX, UV-visible spectrophotometer and four probe techniques which are explained in our previous articles [21-24].

III. Results and discussion

3.1 Structural properties

The surface morphology details of the CdSe/glassthin films (nanowires and corn-like nanowires) were discussed in our previous publications [24] and similar structures emerged in CdSe/FTOnanowire thin films. However, there are some differences according to the annealing temperatures, the substrate (FTO) and the thickness.

The cross-sectional and top surface images of CdSe/FTO nanowire thin films with different magnifications are shown in Figs. 1(a)- 1(e), Figs 2(a)- 2(e), respectively. Figs. 1(a) - 1(f), with different scales and magnification 50.00 KX, show the top surface images of the CdSe/FTO nanowires that obviously exhibit two interesting types of structural feature: elongated nanowires and corn-like nanowires. It was found that the SEM image of the as-deposited and annealed at 373 K, 473 K and 573 K CdSe/FTO nanowire thin films in Figs. 1(a) - 1(d) have elongated nanowire shapes. The SEM images of CdSe/FTO nanowire thin films at annealing temperatures 673 and 773 K in Figs. 1(e)-1(f) turned wholly from nanowire structures to corn-like nanowire structures. The diameter of the CdSe/FTO corn-like nanowire particles are around 20-40 nanometers.

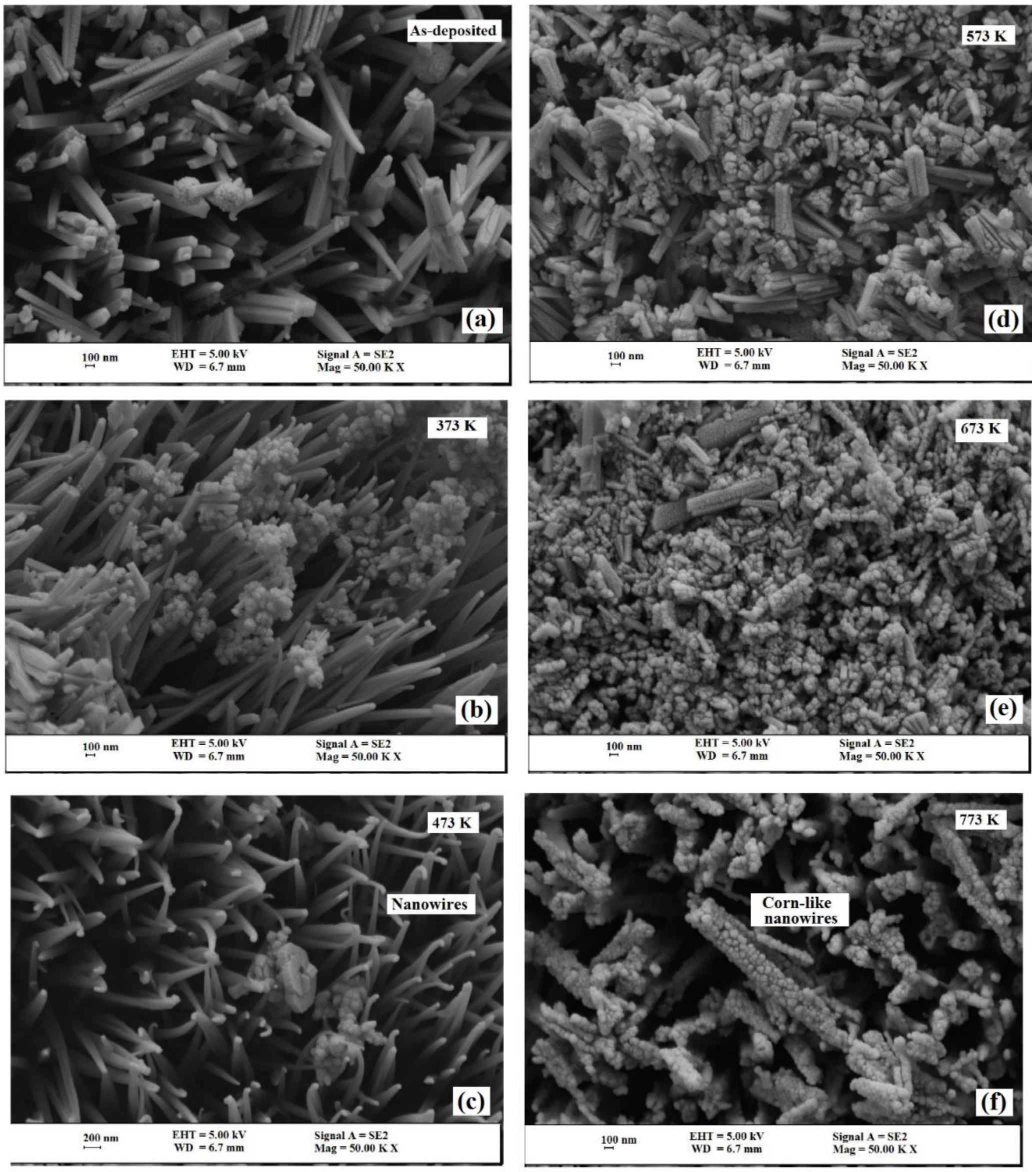

Figure 1. SEM images top surfaces of the CdSe/FTO nanowires (a) as-deposited, and annealed in air atmosphere at (b) 373 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K.

Cross-sectional surface images in Figs. 2(a) - 2(f), with different scales and magnification 75.00 KX show that the nanowires have elongated nanowire shapes. As the cross-sectional surface images of the as-deposited and annealed at 373, 473 and 573 K CdSe/FTO nanowire thin films in Figs. 2 (a) - (d) were examined, all of them were observed to be uniform nanowires. In addition, the CdSe/FTO corn-like nanowire structure is more pronounced in Figs. 1(e) - 1(f) than in Figs.2 (e) - 2(f). Also, the CdSe/FTO corn-like nanowires have lengths and diameters ranging from 900 nm to 2.4 µm and from 70 nm to 165 nm, respectively.

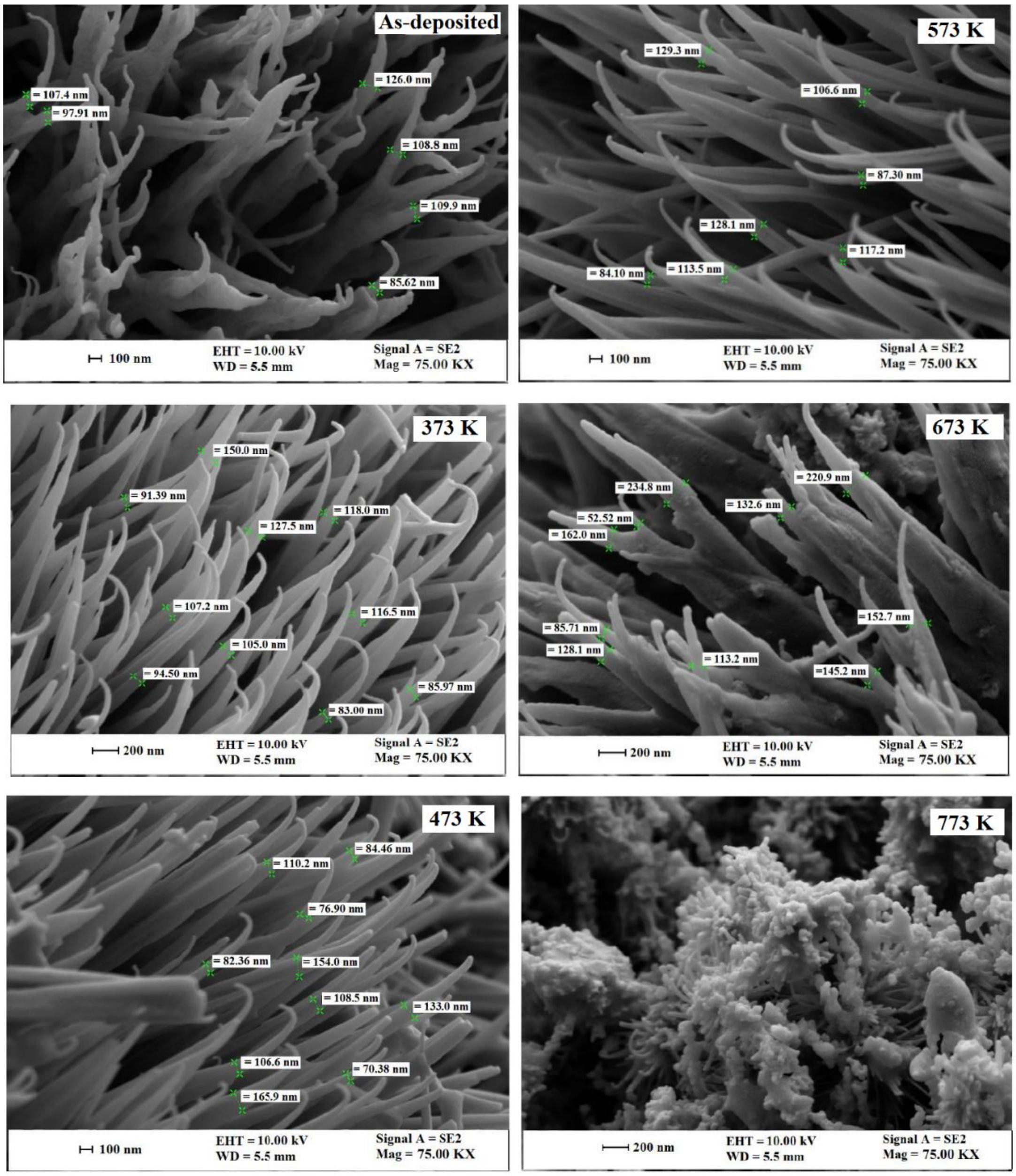

Figure 2. SEM images cross-sectional surfaces of the CdSe/FTO nanowires (a) as-deposited, and annealed in air atmosphere at (b) 373 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K.

Moreover, examining these micrographs showed that the shape of the CdSe/FTO nanowires at the nanoscale was another decisive factor for the properties, and shape uniform growth of nanowires can find unique applications in electronics and photonics. CdSe/FTO nanowires were of particular interest compared to other nano materials due to their asymmetric shape such as rapid carrier transport, in the long direction. CdSe/FTO nanowires and corn-like nanowires have a higher absorption cross-section, allowing for more efficient harvesting of light per particle. More efficient light harvesting is an important factor in improving the solar cell performance. Also the higher absorption efficiency allows for less CdSe nanowire to be used in constructing the photovoltaic, leading to a reduction in device cost [25].

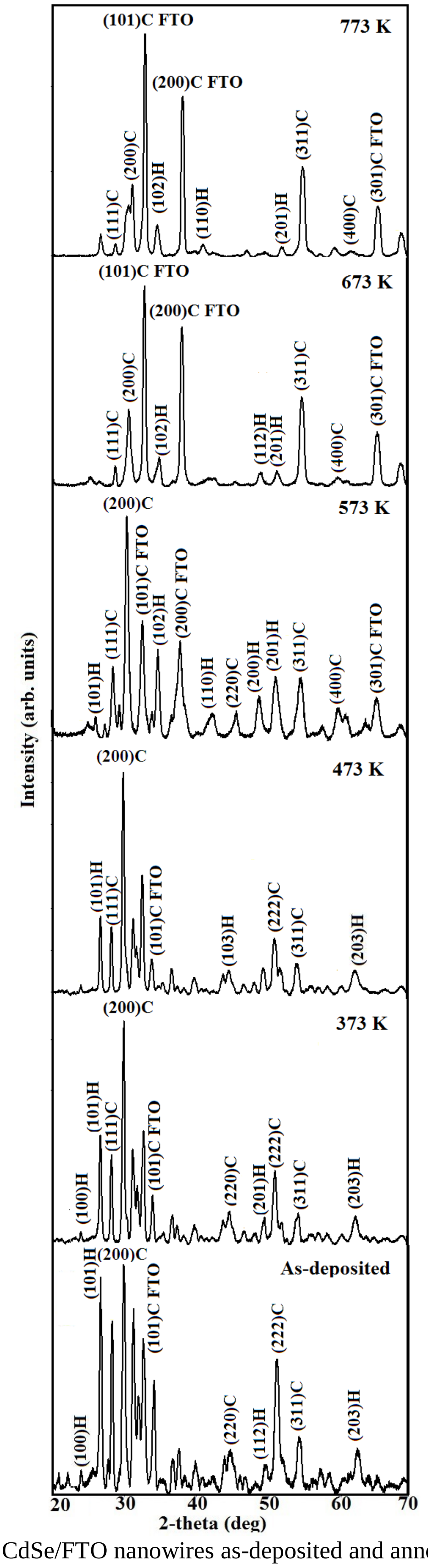

Figure 3. X-ray diffractograms of the CdSe/FTO nanowires as-deposited and annealed in air atmosphere.

To determine the structural properties of the as-deposited and annealed at 373, 473, 573, 673 and 773 KCdSe/FTO nanowireand corn-like nanowire thin films, XRD patterns were analyzed.The XRD patterns of the as deposited and annealed CdSe/FTO nanowireand corn-like nanowire thin filmsshowed well-defined peaks indicating bothcubic (zincblend) and hexagonal (wurtzite) structure in Fig. 3.All the reflections matched well with the standard JCPDS (JointCommittee on PowderDiffractionStandards) data. Using the standard “d” of CdSe corn-like nanowireand corn-like nanowirethin films which were given by cubic (C) [26-28] and hexagonal (H) [29-31], the plane indices of the observed “d”were obtained.Annealing the CdSe/FTO nanowire thin films at 373 K and 473 K increased the intensity of almost all peaks, without any phase conversion. From the figure we noticed that as the annealing temperature of films was increased from 573 K to 773, the peak intensity and peak numbers of the substrate (FTO) started to increase which shows that the CdSe/FTO corn-like nanowire thin films were thinned with increasing annealing temperature. The peak widths at half maximum (FWHM) of the (200) C plane of all films were found to be similar, indicating that all have nanocrystallites of the nanowires. The diffraction pattern with somewhat dispersed and elongated spots implies that the CdSe/FTO nanowires and corn-like nanowires grew with uniform nanocrystal structure nearly parallel to each other. The results of X-ray analysis agreed well with earlier reports [23, 32-34].

3.2 Optical properties

The optical transmission measurements of the as-deposited and annealed CdSe/FTO nanowire and corn-like nanowire thin films were carried out by UV-Visible spectrophotometer. All the measurements were made at room temperature. The terms used to determine the thickness and absorption of films were given in our previous studies [23]. Extrapolation of the nonlinear plot of α^2 (absorption) versus hv (photon energy) in Fig. 4 show the bandgaps (Eg) of the as-deposited and annealed CdSe/FTO nanowire and corn-like nanowire thin films. The bandgaps of the films were given in Table 1. It was observed that the energy band gap decreased from 1.84 eV to 1.53 eV as a result of the shift of the absorption edge of the annealed films towards low energy with increasing annealing temperature, which agrees well with earlier studies [21-24]. As the annealing temperature was increased, the lengths and diameters of CdSe/FTO nanowire and corn-like nanowire thin films also increased as a result of the decrease in the band gap.

The CdSe nanowire thin films are particularly attractive for solar application due to the fact that they are a direct bandgap semiconductor with good overlap of the solar spectrum, with the band edge extending from 650 to 720 nm depending on the diameter. This allows for the nanowire to serve as a sensitizer in addition to a charge carrier transporter when constructing a nanowire solar cell.

Table 1. The optical bandgapand activation energy of the CdSe/FTO nanowiresas-deposited and annealed in air atmosphere.

Annealing temperature (K)	E_g (eV)	LR (meV)	HR (meV)
As-deposited	1.84	6.65	3.23
373	1.83	2.20	5.00
473	1.66	2.10	1.09
573	1.53	1.98	1.63
673	1.54	1.26	3.86
773	1.57	0.70	5.26

LR: Lowtemperatureregionand HR: High temperatureregion

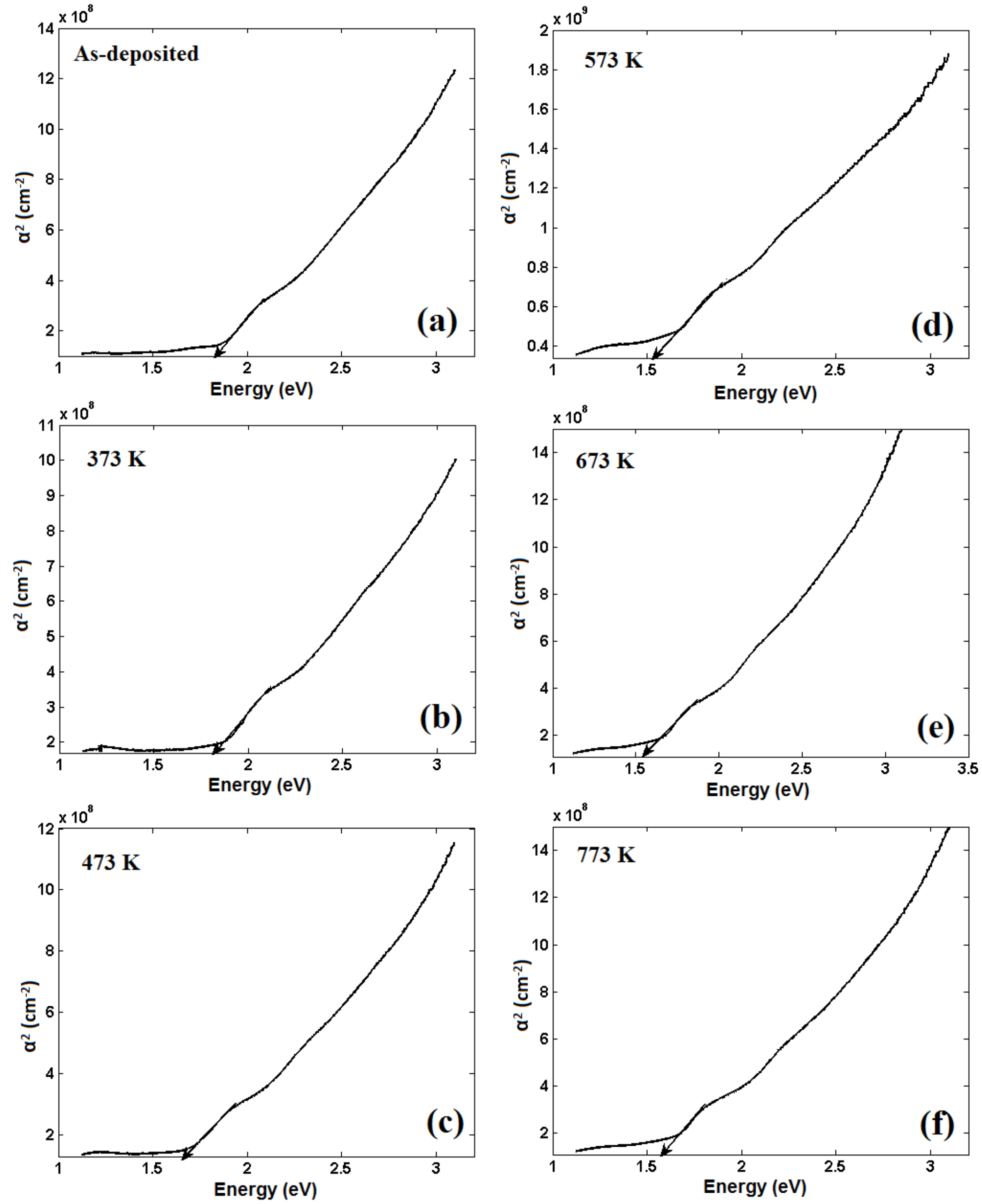

Figure 4. The α^2 versus hν for the CdSe/FTO nanowires as-deposited and annealed in air atmosphere at (b) 373 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K.

3.3 Electrical properties

The results of electrical resistivity of the all filmswere obtained with conducted in the temperature range 310 K– 680 K on rectangular-shape samples with typical 20.0 mm^2, using a standard direct current (DC) four-point probe method. The details of this method are discussed in our previous publication [23].

The temperature dependence of electrical resistivity of the as-deposited and annealed CdSe/FTO nanowire thin films was shown in Fig. 5. The room temperature resistivity's of the thin films were of the order of $12x10^6$ Ω cm and agreed with the published value of $6.0x10^6\Omega$ cm [7]. The electrical measurement results showed that the electrical resistivity of the as-deposited and annealed CdSe/FTO nanowire thin films decreased from 3.52 x $10^4\Omega$ cm to 1.27 x $10^3\Omega$ cm with increasing annealing temperature at 668 K. Electrical measurement results indicated that the samples have shown typical semiconductor characteristics.

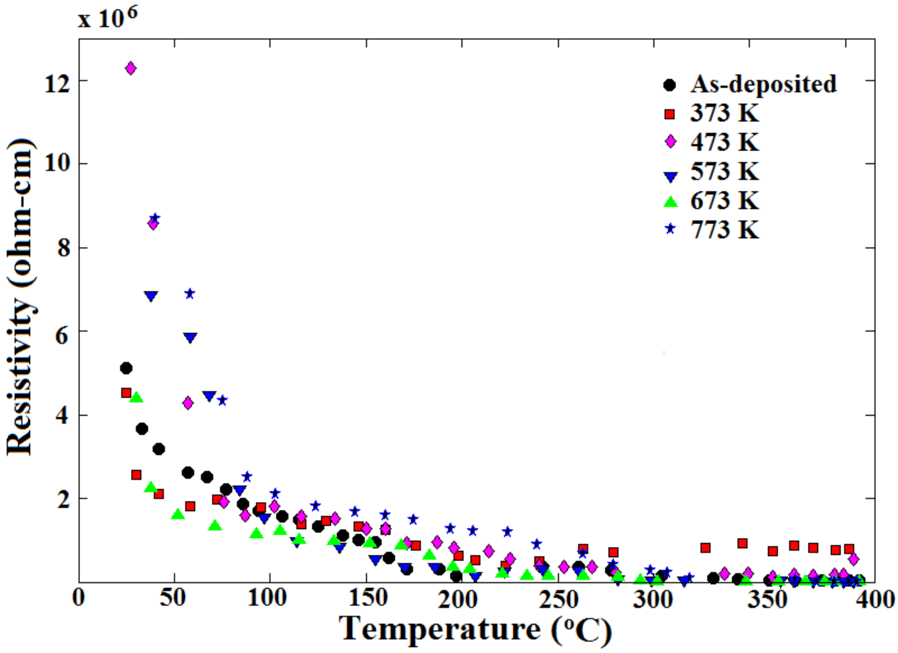

Figure 5. The temperature dependence of the electrical resistivity of the CdSe/FTO nanowires as-deposited and annealed in air atmosphere.

The electrical conductivities of the samples were also calculated from the electrical resistivity values using standard conversion equation. The room temperature resistivity was found to be about $12x10^6\Omega$ cm. The high value of the room temperature resistivity is attributed to the dislocations and imperfections of the films. The electrical resistivity of the chemically deposited CdSe/FTO nanowire thin films was used for calculating the activation energy. The activation energy of dark resistivity was calculated by using the relation

$$\rho = \rho_0 \exp(E_a / kT)$$

and plotting $\ln(\rho / \rho_0)$ versus *1/T* (K), where ρ is the electrical resistivity at temperature *T*, ρ_o is the resistivity at room temperature, *k* is the Boltzmann constant and E_a is the activation energy. Activation energy was found in two different regions from the slope of $\ln(\rho / \rho_0)$ versus *1/T* (K) plot. It was observed to decrease from 6.65 meV to 0.70 meV with increasing annealing temperature in the low temperature region (LR). Whereas, there were increases and decreases in the activation energy with increasing annealing temperature in the high temperature region (HR). The activation energies of the thin films are given in the Table 1.

IV. Conclusions

The CdSe thin films were deposited on FTO substrates by chemical bath deposition (CBD) at 70 °C and annealed in an air atmosphere at different temperatures. According to SEM images, the films had the shape of elongated nanowire and the shapes were changed to corn-like nanowire structures with annealing at higher temperatures, 673 and 773 K, in air atmosphere. Also, the lengths and diameters of CdSe nanowires increased with increasing annealing temperature. XRD results showed that the thicknesses of films decreased with increasing annealing temperature by virtue of evaporating of Cd and/or Se atoms. Furthermore, the electrical resistivity of films decreased with increasing annealing temperature at 668 K. Many researchers think that nanowires enable production of more efficient solar cells. The nanowires are of particular interest because of their unusual properties such as tunable optical and electrical properties. Consequently, these properties can allow the fabrication of low cost, high efficiency nanowire solar cells.

Acknowledgements

The authors would like to thank Mersin University because of that this study was supported by Mersin University Scientific Research Unit (agreement contract: BAP-FEF FB (FS) 2014-2 YL, 2017-2-TP3-2593).

References

[1]. Dasgupta N P, Sun J, Liu C, Brittman S, Andrews S C, Lim J, Gao H, Yan R and Yang P2014 25th anniversary article:semiconductor nanowires–synthesis, characterization, and applications *Advanced mater.***14** 2137-84

[2]. Shi Y, Li H, Wang L, Shen W.and Chen H 2012 Novel Fe2O3/CdS Cornlike Nanorods with Enhanced Photocatalytic Performance *Appl. Mater. Interfaces* **4** 4800-06
[3]. Wang D, JakobsonH P, Kou R, Tang J, FinemanR Z,Yu D.and Lu L2006 Metal and Semiconductor Nanowire Network Thin Films with Hierarchical Pore Structures*Chem. Mater.* **18** 4231-37
[4]. Xia Y, Yang P, Sun Y,Wu Y,Mayers B, Gates B, Yin Y, Kim F and Yan H 2003 One-Dimensional Nanostructures: Synthesis, Characterization, and Applications*Adv. Mater.***15** 353-89
[5]. Yang P, Yan R and Fardy M 2010 Semiconductor Nanowire: What's Next? *Nano Lett.* **10** 1529-36
[6]. Piccione B, Vugt L K Vand Agarwal R2010 Propagation Loss Spectroscopy on Single Nanowire Active Waveguides,» *Nano Lett.***10** 2251-56
[7]. Bakiyaraj G.and Dhanasekaran R 2012 Effect of annealing on the properties of chemical bath deposited nanorods of CdSe thin films *Cryst. Res. Technol.* **9** 960-66
[8]. Khalkhali M, Liu Q, Zeng Hand Zhang H 2015 A size-dependent structural evolution of ZnS nanoparticles*Scientific reports***5**14267
[9]. Zhao Y, Yan Z, Liu Jand Wei A 2013 Synthesis and characterization of CdSe nanocrystalline thin films deposited by chemical bath deposition*Materials Science in Semiconductor Prosessing* **16** 1592-98
[10]. Kale R Band Lu S Y2015 Air annaeling induced transformation of cubic Cdse microspheres into hexagonal nanorods and micro-pyramids*Journal of Alloys and Compounds***640** 504-10
[11]. Gopakumar N, Anjana P Sand Vidyadharan Pillai P K 2010 Chemical bath deposition and characterization of CdSe thin films for optoelectronic applications*J MaterSci***45** 6653-56
[12]. Farva U and Park C 2010 Influence of thermal annealing on the struvtural and optical properties of CdSe nanoparticles*Solar Energy Materials & Solar Cells* **94** 303-09
[13]. Esparza-Ponce H E, Hernandez-Borja J, Reyes-Rojas A, Cervantes-Sanchez M, Vorobiev Y V, Ramirez-Bon R, Perez-Robles J Fand Gonzalez-Hernandez J 2009 Growth technology, X-ray and optical properties of CdSe thin films*Materials Chemistry and Physics***113**,824-28
[14]. Desphande M, Garg N, Bhatt S V, Sakariya Pand Chaki S2013 Characterization of CdSe thin films deposited by chemical bath solutions containing triethanolamine *Materials Science in Semiconductor Processing***16**915-22
[15]. Chate P, Hankare Pand Sathe D2010 Characterization of cadmium selenide films for photovoltaic applications *Journal of Alloys and Compounds***505**140-43
[16]. Chate P, Sathe D, Hankare P, Lakade S and Bhabad V2013 Synthesis and characterization of cubic cadmium selenide by chemical route *Journal of alloys and Compounds* **552** 40-43
[17]. Kois J, Gurevits J, Bereznev S, Volobujeva O, Öpik AandMellikov E2013 CdSe nanofiber and nanohorn structures on ITO substrates fabricated by electrochemical deposition *Applied Surface Science* **283**982-85
[18]. Erenturk B, Gurbuz S, Corbett R E, Claiborne S A M, Krizan J, Venkataraman Dand Carter K R 2011 Formation of Crystalline Cadmium Selenide Nanowires *Chem. Mater.***23** 3371-76
[19]. Dong L, Niu S, Pan C,Yu R, Zhang Y and Wang Z L 2012 Piezo-Phototronic Effect of CdSe Nanowires*Adv. Mater.***24** 5470-75
[20]. Mahato S, Shakti N and Kar A 2015 Annealing temprature dependent structural and optical properties of electrodeposited CdSe thin films*Materials Science in Semiconductor Processing* **39** 742-47
[21]. Metin H,Erat Sand Bozoklu M 2008 Characterization of CdSe films prepared by chemical bath deposition method *Optoelectronics and Advanced Materials* **2** 92-98
[22]. Metin Gubur H, Septekin F and Alpdogan S 2015 CdSe Nanowires Grown by Using Chemical Bath Deposition *Journal of the Korean Physical Society***7** 1222-27
[23]. Erat S, Metin HandArı M 2008 Influence of the annealing in nitrogen atmosphere on the XRD, EDX, SEM and electrical properties of chemical bath deposited CdSe thin films *Materials Chemistry and Physics* **111**114-20
[24]. Metin Gubur H, Septekin F, Alpdogan S, Sahan Band Kesik Zeyrek B2016 Structural properties of CdSe corn-like nanowires grown by chemical bath deposition *J Mater Sci:Mater Electron***7** 7640–45
[25]. ProtasenkoV,Bacinello D andKuno M. 2006 Experimental determination of the absorption cross-section and molar extinction coefficient of CdSe and CdTe nanowires. *The Journal of Physical Chemistry B***110** 25322-31.
[26]. JCPDS, PowderDiffraction Data (PDF Card No: 077-7287).
[27]. JCPDS, PowderDiffraction Data (PDF Card No: 073-6987).
[28]. JCPDS, PowderDiffraction Data (PDF Card No: 071-4157).
[29]. JCPDS, PowderDiffraction Data (PDFCard No: 002-0330).
[30]. JCPDS, PowderDiffraction Data (PDF Card No: 075-5679).
[31]. JCPDS, PowderDiffraction Data (PDF Card No: 077-2307).
[32]. KaleR B and LuS Y 2015 Air annealing induced transformation of cubic CdSe microspheres into hexagonal nanorods and micro-pyramids*Journal of Alloys and Compounds***640** 504-10
[33]. Khomane A S 2011 Structural and optical characterizations of chemically deposited cadmium selenide thin films *Materials Research Bulletin***46** 1600-3
[34]. Singh A K, Deo S R, Thool G S, Singh R S, Katre Y R and Gupta A 2011 Synthesis and characterization of chemically deposited nanocrystalline CdSe thin film*Synthesis and Reactivity in Inorganic,Metal-Organic, and Nano-Metal Chemistry* **10**1346-50

HulyaMetinGubur"Effect of Annealing Temperature on the CdSe/FTO (SnO2:F) Nanowires Grown by Chemical Bath Deposition.” IOSR Journal of Applied Physics (IOSR-JAP) , vol. 10, no. 4, 2018, pp. 07-14.