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EFFECT OF ELECTRON BEAM IRRADIATION ON NANOSTRUCTURED COPPER TELLURIDE THIN FILM

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Abstract

As deposited Copper telluride flower like microstructures constructed by quantum dots with various diameters were obtained by potentiostatic electrodeposition method. The electrolyte concentration and deposition time can be used to control the diameter of the electrodeposited quantum dots to within the range of 50-65 nm. As deposited films are found to be stoichiometric in composition. The thin films are prepared using electrodeposition technique at room temperature and irradiated with electron beam of 2Mev. The surface morphology of film shows drastic change after irradiation. Onion flower like structure with quantum dots changes to coli flower like structure with quantum dots within the range of 20-25 nm. The optical constants such as optical band gap energy and optical absorption spectra shows significant variation in their values with electron beam irradiation. Upon irradiation the band gap energy increased from a value of 2.74eV to 2.88 eV and 2.89 eV to 3.01eV. The structural, optical, surface morphology, compositional analysis and Raman spectra properties of the irradiated films have been studied.

Keywords :*Electrodeposition, irradiation, copper telluride, quantum dots, Chemical composition, Optical properties,*

Short Profile

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INTRODUCTION

Chemical methods are very attractive, since they are relatively simple, low cost and convenient for larger area deposition of thin films. Copper telluride forms different phase's viz. CuTe, $Cu_{2-x}Te$, Cu_2Te etc. CuxTe thin films have been found to possess near ideal solar control characteristics. Generally the films are blackish gray-blue-purple-red in color. The Cu_xTe thin films may be used in photo-detectors and in photovoltaic applications. $Cu_{(2-X)}Te$ nanowires synthesized by a microwave-assisted solvothermal method using a self-sacrificial template and their electrical conductivity [1]. There has been increasing interest during the past few decades in semi-conducting copper chalcogenide thin flms because of its wide range of applications in various fields of science and technology. Copper chalcog enide thin films have a number of applications in various devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroc-onductive electrodes, microwave shielding coating, etc. [2-6]. Copper telluride belongs to copper chalcogenide (group's I-VI compou nd) materials. Controlled hydrothermal synthesis and growth mechanism of various nanostr- uctured films of copper and silver tellurides is explai- ned [7]. Deposition of metal chalcog- enide thin films by successive

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ionic layer adsorption and reaction (SILAR) method is reported [8]. Preparation and characterization of copper telluride thin film by modified chemical bath deposition (M-CBD) method is also reported [9]. Hydrophilic nature of electrodeposited copper telluride and stress, mass, fringe width and thickness of CuTe thin film is reported [10]. Large-scale synthesis of transition metal chalcogenide in its nanoregime by an element-directed, less hazardous, template-free, inexpensive aqueous solution method and films with homogeneous green luminescent copper telluride (Cu_2Te) nanoparticles have been synthesized in a single reaction at 70°C within 9 h by a wet chemical method [11], this method ensures almost complete utilization of the precursors with a very high productive yield. Polycrystalline Cu_7Te_4 dendritic microstructures were successfully synthesized via a simple galvanostatic electrochemical deposition method at room temperature [12]. Cu_7Te_4 microstructure constructed by nanoparticles, synchronized isolation of aliquots of Cu_2Te nanoparticles with defined sizes of 25- 30 nm is also reported [11,12]. The electrodeposition of Cu, Te and Cu-Te thin films on BDD electrodes was investigated [13]. The structural and electronic properties of the novel semiconductor alloy $Cd_{1-x}Cu_xTe$ is determined [14]. The study of copper telluride (Cu_2Te) nanostructures (nanowires) of 100 nm diameter have been fabricated using electrodeposition method from an aqueous solution on copper (Cu) and indium tin oxide (ITO) substrates [15].

1.2. EXPERIMENTAL

1.2.1 Film Growth

The Cu_2Te quantum dots were synthesized at room temperature by electrode position method. Room temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical deposition results in pin hole free and uniform deposits are easily obtained since the basic building blocks are ions instead of atoms. Preparative parameters such as deposition time, and concentration of precursor were optimized. In the typical synthesis, (0.1 M) copper sulphide ($CuSO_4$) and (0.005M) sodium telluride (Na_2TeO_3), are used as source of copper and Telluride respectively while triethanolamine is used as complexing agent. Solutions are prepared in double distilled water. The ultrasonically cleaned stainless steel and ITO substrate are used to prepare samples. All reagents were of analytical grade and used without further purification. Copper telluride thin films were prepared on stainless steel, ITO substrate by electrodeposition technique. Electrolytic bath contains 12 ml $CuSO_4$ and 12 ml as Na_2TeO_3 as sources of Cu and Te ions and 6ml of triethanolamine as complexing agent. Electrodeposition study of Cu_2Te thin films was made using potentiostat (Princeton Perkin-Elmer, Applied Research Versa-stat-II; Model 250/270) in three-electrode configuration. Pure graphite plate was used as an anode, stainless steel was used as cathode and saturated calomel electrode (SCE) was used as reference electrode. Blackish-gray colored, smooth, uniform Cu_2Te thin films were obtained. In present work it is to be observed that by keeping conc. fixed and changing deposition time the excess of copper decreases with increase in deposition time and thin films become more adhesive and stoichiometric. At 15 min. deposition time shows more stoichiometry. Optimised films are irradiated with electron beam irradiation unit at BARC Mumbai.

1.3 RESULTS AND DISCUSSION

1.3.1 X-RAY DIFFRACTION

The XRD pattern of the as deposited Cu_2Te samples for bath concentrations 0.10 M $CuSO_4$ and 0.005M sodium telluride with deposition time of 15 min. is shown in fig.1 (a). Figure indicates the formation of polycrystalline Cu_2Te, and all of them can be indexed as the reported hexagonal Cu_2Te (JCPDS No. 39-1061).

Diffraction peaks of other phases or impurities were not detected, further confirming that the precursors have been completely transformed into Cu_2Te quantum dots. Table.1 shows the comparison of measured and standard d values for the films deposited with solution concentrations 0.10M $CuSO_4$ and 0.005M sodium telluride and deposition time of 15min. They are in good agreement with standard d values. Hence the copper telluride present in the structure of quantum dots is hexagonal. The phases of copper telluride can be easily distinguished by the powder X-ray diffraction pattern, all of the peaks can be indexed as (103), (201), (203), (300) and (302) in the hexagonal Cu_2Te structure. The calculated lattice constants a=4.2370 and c=7.2740K are in agreement with the standard literature values (JCPDS No. 39-1061). The XRD pattern of the irradiated Cu_2Te samples for bath concentrations 0.10 M $CuSO_4$ and 0.005M sodium telluride with deposition time of 15 min. is shown in fig.1 (b). We conclude that the films are composed of pure copper telluride. The intensity of peak goes on decreases with electron beam irradiation, indicates decrease in crystallinity of material shown in fig. 1(b).

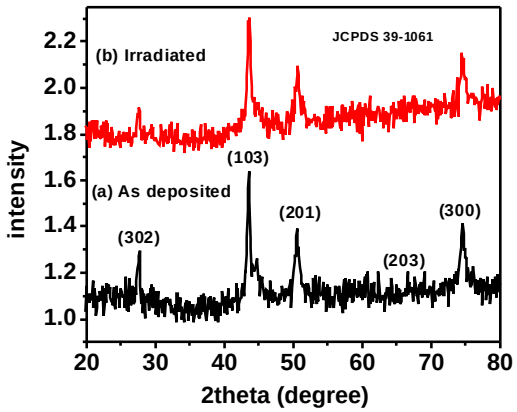
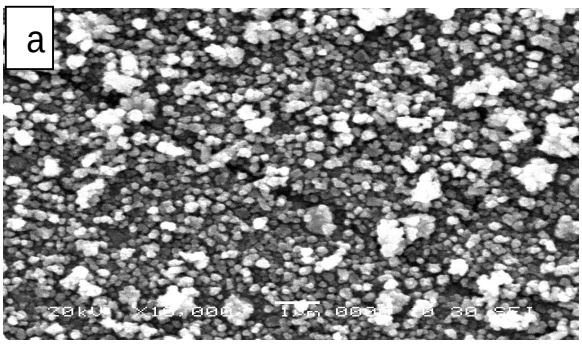
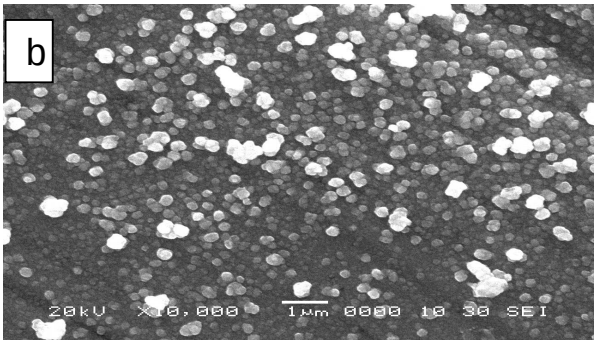


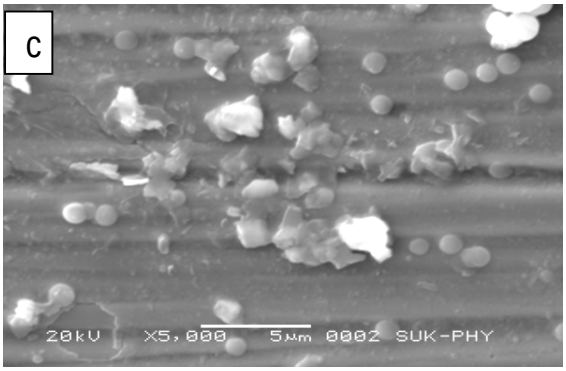
Figure.1 XRD pattern of Cu_2Te with bath concentration of 0.10M $CuSO_4$ and 0.005M Na_2TeO_3 (a) As deposited with deposition time 15 min (b) Irradiated with deposition time 15 min.

1.3.2 Scanning electron microscope:

The morphology and nanostructure of the resulting copper telluride films were investigated by using scanning electron microscopy (SEM). Fig.2 (a,b) shows that different copper telluride nanostructures were obtained by varying the deposition time. These nano-sized dots possess over whole surface, these quantum dots are of 50nm-100nm in diameter. The well developed and matured Cu_2Te quantum dot with onion flower like structure growths were shown in FESEM images fig. 2(a-c). SEM images of Cu_2Te after irradiation are shown in fig.2 (b,d) From these figure it is to observed that the substrate surface of thin film is defected and all quantum dots are become smaller in size with 20nm-25nm in diameter.







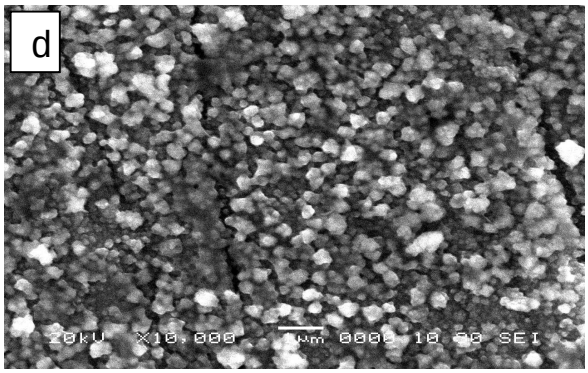
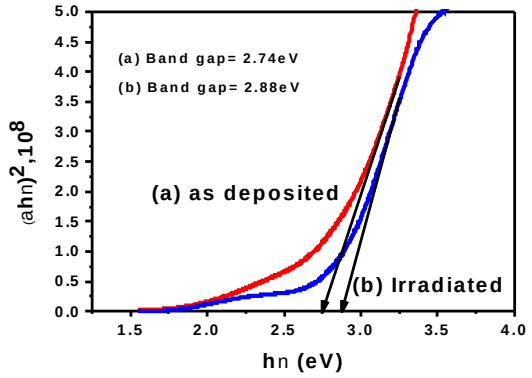


Figure.2 SEM images of Cu_2Te with bath concentration of 0.10M $CuSO_4$ and 0.005M Na_2TeO_3 (a) as deposited with deposition time 10 min (b) irradiated with deposition time 10 min(c) as deposited with deposition time 15 min (d) irradiated with deposition time 15 min

1.3.3 Optical properties:

The optical band gap energy was determined from the plot of $(\alpha h\nu)^2$ (a is the absorption coefficient calculated from transmission data) versus photon energy in the visible region as shown in fig.3(a,b,c,d) for bath concentrations 0.10M $CuSO_4$ and 0.005M sodium telluride and deposition time of 10min and 15min.. Band gap energy was calculated from the classical relation for direct-band optical absorption. The optical band gap of as deposited Cu_2Te films estimated from the fig.3(a,c) is 2.79 eV for 10 min. deposition time, 2.89eV for 15 min deposition time and the optical band gap of irradiated Cu_2Te thin films is 2.88 eV for 10 min. deposition time, 3.01 eV for 15 min deposition time. Optical band gap increases with electron beam irradiation these optical band gap values are nearly equal with reported values [11,15]. After irradiation increase in band gap takes place due creation of new energy levels. The increase in the optical band gap energy and appearance of second band gap after irradiation implies the creation of additional energy levels. Such additional levels could be mostly due to the creation of deep trap states. There is a tendency that more telluride-rich films have a higher band gap. The change in the band gap with size (quantum dots) shows the blue shift in copper telluride quantum dots which can be attributed to the quantum size effect in coli flower like structure [15]. The optical properties such as absorption coefficient, energy band gap play an important role in understanding the optoelectronic properties of semiconducting materials.



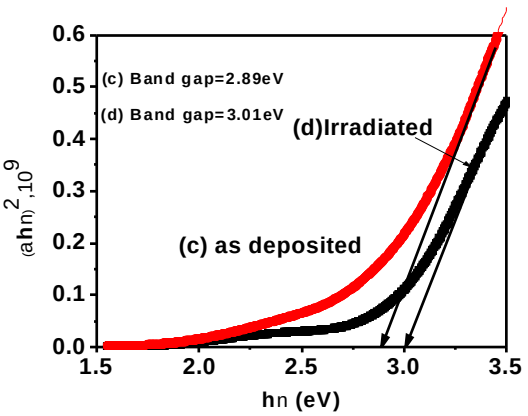


Figure.3 Optical band gap of Cu_2Te with bath concentration of 0.10M $CuSO_4$ and 0.005M

Na_2TeO_3 (a) as deposited with deposition time 10 min.(b) irradiated with deposition time 10 min
(c) as deposited with deposition time 15 min.(b) irradiated with deposition time 15 min

CONCLUSIONS:

It is concluded that, as deposited and irradiated copper telluride (Cu_2Te) thin films successfully deposited by electrodeposition technique. X-ray studies showed that as deposited and irradiated films are polycrystalline in nature. Surface morphology of as deposited films shows that crystals are hexagonal, with increase in concentration of telluride they turn into quantum dots with 50-100 nm. After irradiation there is defect in substrate surface and quantum dots with 20nm-25nm are observed, which is in agreement with XRD. The band gap of copper telluride depends on their stoichio metries. Band gap energy is higher with rich telluride and decreases with copper. The Optical band gap of irradiated Cu_2Te thin film changes from 2.74eV to 2.88 eV and 2.89 eV to 3.01eV. The optical properties of such films make them suitable for solar control coatings and photovoltaic devices. The electrodeposition method is constructive for preparation of large area quantum dots after irradiation.

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