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Research Article

ANNEALING EFFECTS ON CdHgTe THIN FILMS: ADJUSTING Hg CONTENT AND ENHANCING CRYSTAL QUALITY

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Abstract: This study explores the electrodeposition of CdHgTe thin films using a complex electrochemical bath comprising $CdCl_2$, $HgCl_2$, and pre-reacted metallic tellurium in concentrated nitric acid, with acetonitrile as a complexing agent. The films are deposited on SnO_2 coated glass substrates using a three-electrode system, where deposition potentials are adjusted to vary Hg content without altering bath composition. After deposition, films undergo annealing at 300°C under rough vacuum conditions, enhancing crystalline quality and X-ray diffraction peak intensity. Results show that deposition at different potentials affects film quality, with annealing mitigating deterioration observed at more negative potentials. Structural analysis reveals cubic (fcc) crystal structure with predominant (111) orientation, unaffected by annealing temperature up to 300°C. This approach offers a novel, cost- effective method to tailor CdHgTe film properties, crucial for various optoelectronic applications.

Keywords: Electrodeposition, CdTe, Thin Films, Cyclic Voltammograms, CH_3CN

Introduction

Mercury Cadmium Telluride ($Hg_xCd_{1-x}Te$) stands out as a significantly important alloy system in the realm of technology due to its precisely tailored characteristics[1]. It stands among the semiconductors that have undergone extensive examination. The inherent direct bandgap of HgCdTe and its tailor made properties[2] contributes to a notably high absorption coefficient. Presently, thin coatings of HgCdTe serve diverse purposes including nuclear radiation sensing, modulation of electro-optical signals, infrared detection, X-ray imaging apparatus, solar cells, and various optoelectronic tools[2–4].

In the realm of thin film deposition techniques for CdHgTe, several approaches have been explored depending on the specific requirements of the application and the equipment available, each with its unique set of advantages and drawbacks. Some common techniques for depositing thin films of HgCdTe are Molecular Beam Epitaxy (MBE)[5,6], Metal organic chemical vapour deposition (MOCVD), Sputtering[7–9], Liquid Phase Epitaxy (LPE)[10], Solution growth technique[11], Thermal evaporation technique[12], Plasma-enhanced Atomic Layer Deposition[13], Chemical bath deposition (CBD)[14], Electrodeposition[15,16] etc. Many of these methods come with considerable costs, complexity, or the use of hazardous gases, making them less desirable for certain applications.

In this study, the electrodeposition technique was chosen to deposit CdHgTe films due to its numerous beneficial features. Firstly, electrodeposition allows for the growth of uniform films over large areas, even on irregularly shaped surfaces, ensuring versatility in application. Secondly, this method is relatively straightforward and environmentally friendly, offering high material utilization, thus reducing waste generation. Additionally, electrodeposition proves to be an intrinsically inexpensive approach, as it requires minimal starting material purity compared to other techniques. These combined advantages have made electrodeposition increasingly popular in recent years for growing a wide range of binary and ternary alloys and semiconductors, including CdHgTe.

Electrodeposition of mercury cadmium telluride (MCT) thin films has its roots in the late 1960s and early 1970s. Throughout the 1970s and 1980s, researchers refined the electrodeposition process for MCT thin films. They experimented with different electrolytic solutions, deposition parameters, and substrates to optimize the

film's properties and quality. Basol et al. in 1986[2] utilized cathodic electrodeposition to grow thin films of CdHgTe from an aqueous solution containing $CdSO_4$ and Hg_2Cl_2, with Na_2SO_4 as the supporting electrolyte.

Te ions were generated using a Te electrode, and the deposition process was conducted with bandgaps varying from 1.5 eV to 1.04 eV. Ramiro et al. in 1996[19] followed a similar procedure, depositing films within the range of x = 0 to x = 0.1 while maintaining a lower temperature of 80°C. Mori et al. in 1990[20] significantly contributed to the understanding of cathodic electrodeposition chemistry in the Hg-Cd-Te system by employing hydrodynamic voltammetry and photo voltammetry. They emphasized the importance of post-deposition thermal treatment to achieve compositionally uniform films. In 1992 Colyer and Cocivera[21] used a non-aqueous bath with HgI_2, $Cd(ClO4)_2$, and $LiClO_4$ in a polypropylene carbonate supporting electrolyte for film deposition. Their findings revealed that increasing Hg^{2+} content in the films corresponded to an increase in the bath composition. Furthermore, the Hg content in the film was observed to vary with temperature; as temperature increased from 80 to 94°C, the Hg content decreased from 0.14 to 0.07. In 2001 J. Ramiro et al. electrodeposited thin films of mercury cadmium telluride and studied its X-ray photoelectron spectroscopy[22]. In 2007 Chauhan S and Rajaram P, deposited MCT thin films on SnO_2 coated glass substrate[23] with the help of Electrodeposition technique.

In previous research, it has been observed that achieving the desired Hg content in CdHgTe thin films often requires altering the composition of the deposition bath. However, in our current study, we demonstrate a novel approach. We show that it is possible to deposit CdHgTe thin films with varying Hg content without modifying the bath composition. Instead, we achieve this by simply adjusting the deposition potentials within the same bath. This innovative technique not only saves time and effort but also reduces costs significantly. Additionally, our research includes a comparative structural analysis of as-grown and annealed CdHgTe thin films, providing valuable insights into the material properties after the deposition process.

Experimental Details

CdHgTe thin films were fabricated using the electrodeposition technique[23]. The electrochemical bath for the deposition of HgCdTe films was made up of a mixture of aqueous solutions of $CdCl_2$, $HgCl_2$ and metallic tellurium (Te) pre-reacted with concentrated nitric acid. Acetonitrile (CH_3CN) was used as complexing agent. The three-electrode system was employed for both bath study and film deposition. The anode in the experiment was made of platinum while the reference electrode was a saturated calomel electrode. The cathode consisted of transparent conducting SnO_2 thin films, which were coated on glass substrate with the help of chemical vapour deposition technique[24]. Throughout the process the bath was continuously stirred and the cyclic voltammograms were obtained from the bath. After stirring for the certain period, the peaks of all the three ions get merged and a plateau region appeared.

Cyclic voltammetry is a widely used electrochemical technique to study the redox properties of materials, analyse electrochemical reactions and investigate the behaviour of different compounds in solution. It provides valuable information about the electron transfer process and kinetics of electrochemical reactions. Fig. 1 shows the cyclic voltammogram for X = 0.2. Where X is the fraction $Hg^{++}/(Hg^{++} + Cd^{++})$. Here we have used cyclic voltammograms to select the deposition potential. By selecting different potentials within the plateau, large number of CdHgTe films were grown. Various techniques can be employed to characterise such grown films, with x-ray diffraction (XRD) being the most used one for determining the crystallographic structure. XRD utilises the diffraction of X-rays to reveal atomic scale details of the internal structure. Through the measurement and analysis of diffraction spot intensities, the precise position of individual atoms within the

crystal cell can be accurately determined. The structure factor is a crucial factor considered during the process of locating the positions of atoms based on the diffraction intensity.

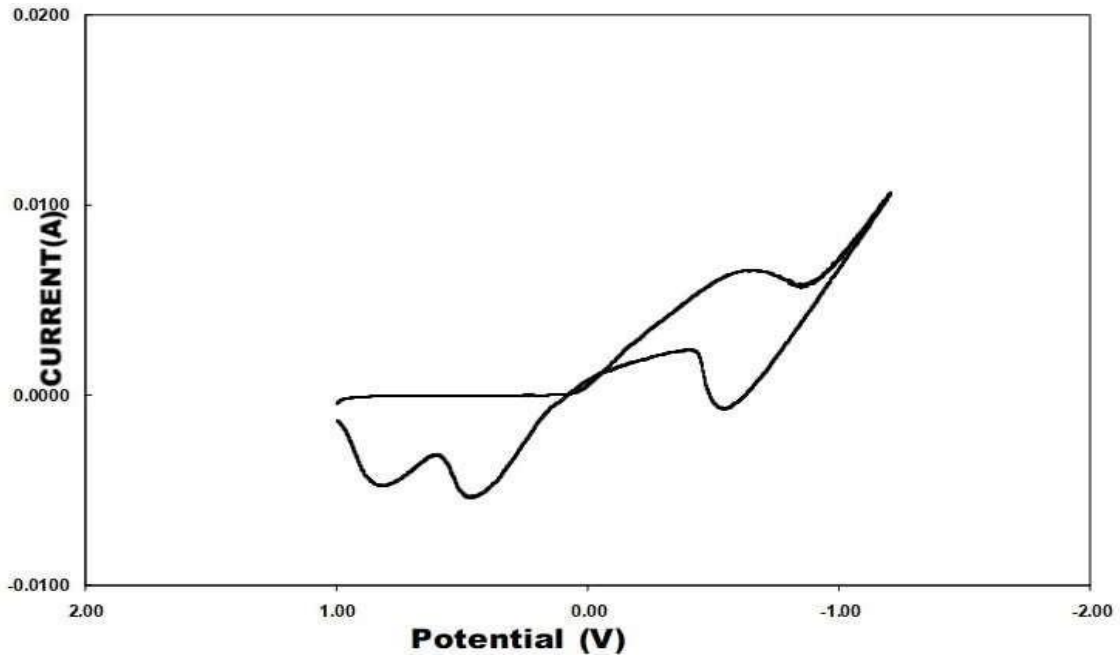

Fig 1. Cyclic voltammogram of the bath having composition X= 0.2

It plays a significant role in the analysis and interpretation of XRD data, allowing researchers to understand the arrangement of atoms in the film and gain insights into its internal structure. Generally, the properties of films are influenced by both the deposition process and post-production steps like annealing. After the growth, the films were subjected to annealing at 300°C in a rough vacuum (10^{-2} - 10^{-3} mm of Hg) for one hour. To identify the different phases, present in the layer, X-ray diffraction (XRD) analysis was performed on the films grown at various deposition potentials from the same bath. The XRD was conducted using a Bruker AXS (Model D-8 Advance) diffractometer with Cu-Kα radiation of 1.5406 Å. Theoretical diffraction data were generated on a computer, utilizing the CdHgTe lattice parameter from ASTM data. To determine thickness, measurements were taken before and after annealing using the Tolansky method. Additionally, Energy Dispersive Analysis of X-rays (EDAX) and optical studies were conducted.

In researches, it has been observed that achieving the desired Hg content in electrodeposited thin films of CdHgTe, often requires altering the composition of the deposition bath. However, our current study presents a novel approach to address this challenge. We demonstrate that it is possible to deposit CdHgTe thin films with varying Hg content without modifying the bath composition, but by adjusting the deposition potential within the plateau region of the cyclic voltammograms. This innovative technique not only saves time and effort but also significantly reduces costs. Furthermore, our research includes a comparative structural analysis of both as-grown and annealed CdHgTe thin films, providing valuable insights into the material properties after the deposition process. This investigation contributes to a better understanding of the film behavior during post-growth treatments, which is crucial for optimizing film quality and performance.

Results and Discussion

In Figure 1, cyclic voltammogram displays a plateau region. By varying the potentials within this plateau, large number of CdHgTe films were produced. The X-ray diffraction analyses of these films, both as-grown and

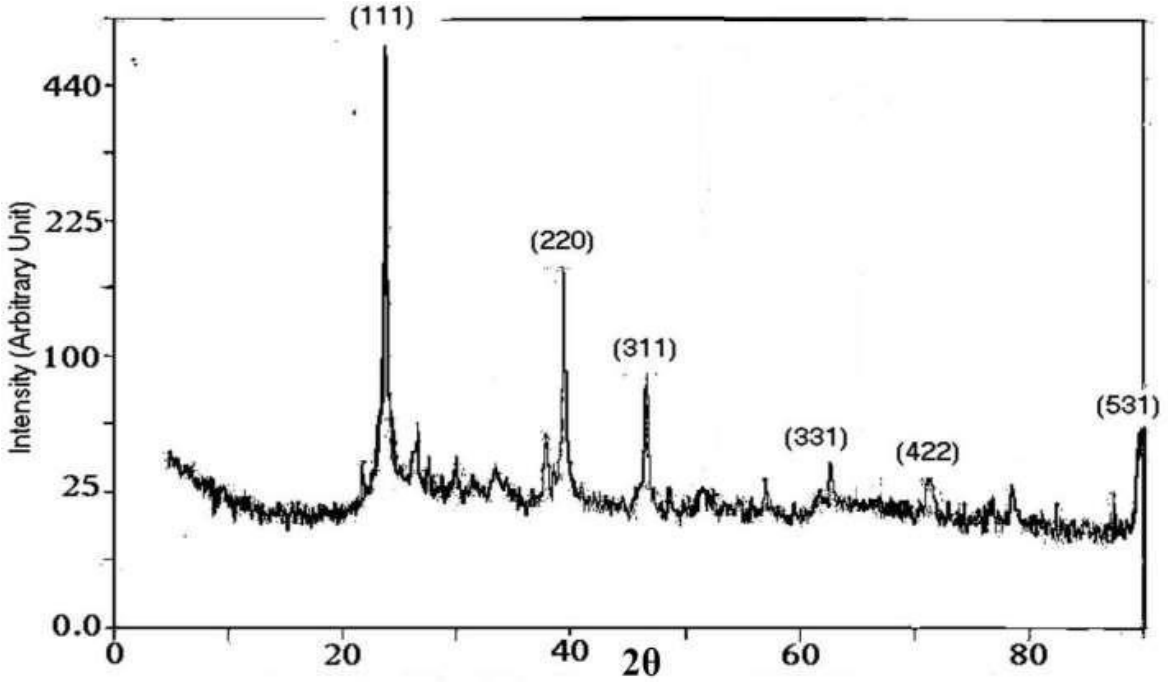

Fig 2. X-Ray diffraction pattern of a CdHgTe film grown at -500 mV w.r.t. SC electrode from the bath of composition X=0.2.

annealed, were conducted, and the observed peaks were identified. The peaks in both cases corresponded to either CdHgTe or the substrate SnO_2. Some experimental patterns exhibited minor additional peaks, which were identified as CdTe, HgTe, or elemental Te. In Figure 2, the X-ray diffraction pattern of as-grown film deposited at -500 mV relative to the Saturated Calomel Electrode from a bath with X = 0.2 composition is presented. The patterns reveal reflections corresponding to CdHgTe, notably (111), (220), (311), (331), (422), and (531), along with SnO_2 peaks from the substrate.

The sharp and intense CdHgTe peaks suggest high-quality, polycrystalline films with a cubic (fcc) structure, predominantly oriented in the (111) direction. Figure 3 showcases the X-ray diffraction pattern of another as-grown CdHgTe film deposited at -600 mV, revealing similar CdHgTe reflections, albeit slightly broadened and less intense, indicating a slight reduction in film quality while maintaining the cubic (111) orientation. Similarly, Figure 4 displays the X-ray diffraction pattern of as-grown CdHgTe films deposited at -700 mV, with broader and weaker CdHgTe peaks, signifying a further decline in film quality. These observations demonstrate that depositing within the plateau region of the cyclic voltammogram results in single-phase HgCdTe deposits. However, shifting the deposition potential towards the negative side of the plateau leads to decreased peak intensities, indicating a decline in film quality. Figure 5 presents the X-ray diffraction pattern of annealed CdHgTe film grown at a deposition potential of -700 mV relative to the saturated calomel electrode.

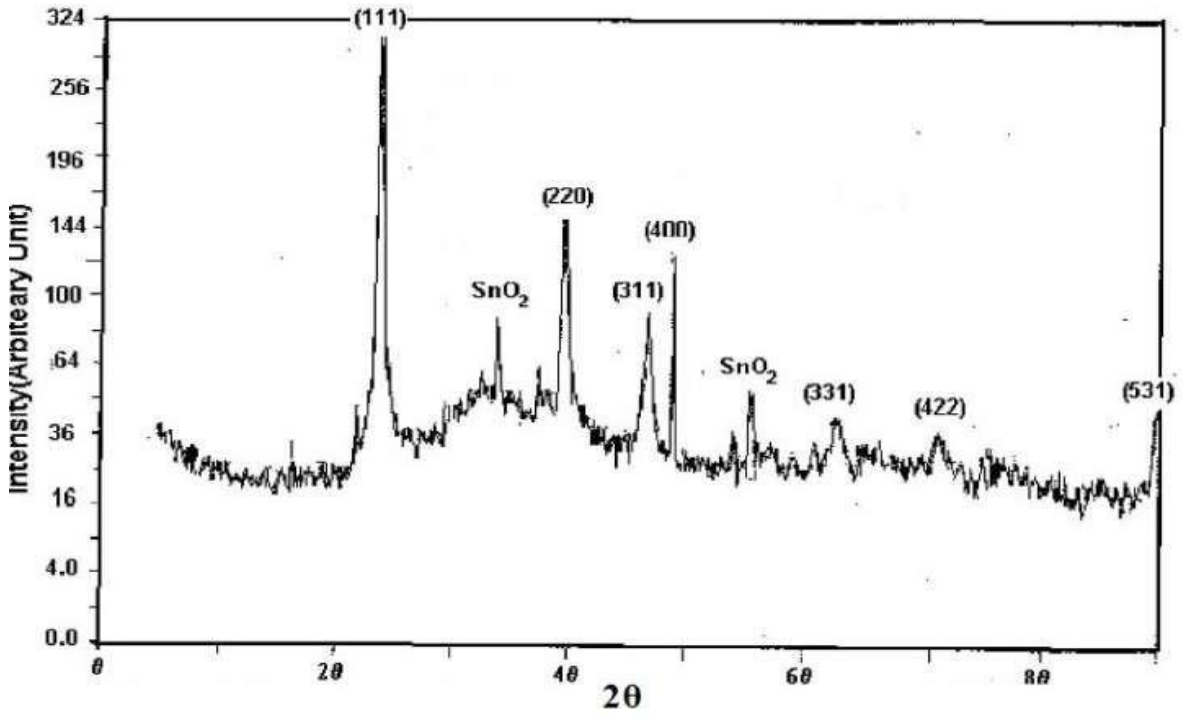

Fig 3. X-Ray diffraction pattern of a CdHgTe film grown at -600 mV w.r.t. SC electrode from the bath of composition X= 0.2

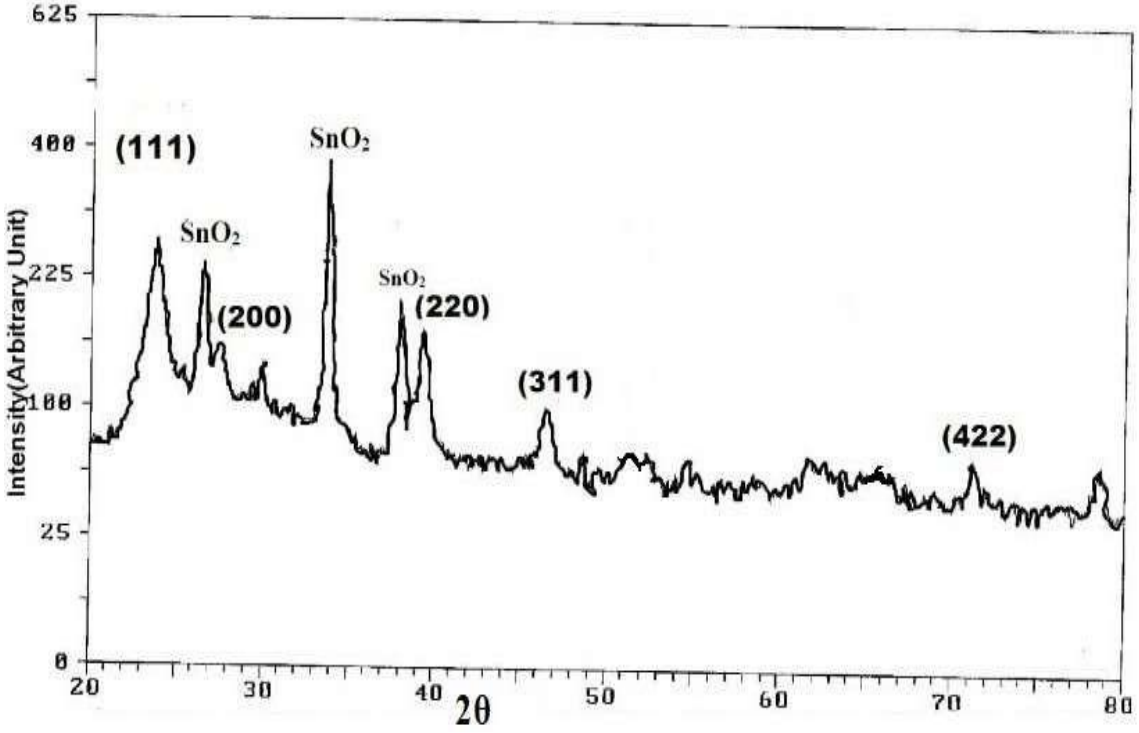

Fig 4. X-Ray diffraction pattern of a CdHgTe film grown at -700 mV w.r.t. SC electrode grown from the bath of composition X= 0.2.

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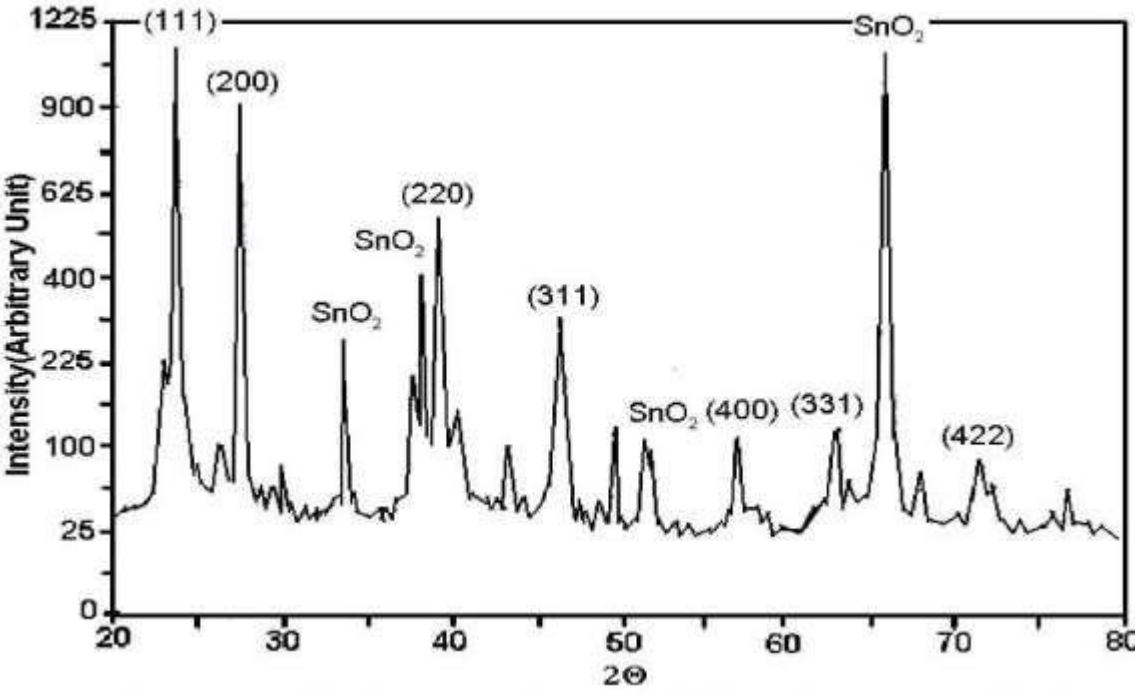

Fig 5. X-Ray diffraction pattern of an annealed CdHgTe film grown at -700 mV w.r.t. SC electrode grown from the bath of composition X = 0.2.

This film underwent annealing at a temperature of 300°C under rough vacuum conditions (between 10^{-2} and 10^{-3} mm of Hg) following its growth. In Figure 4, we see that the peaks of CdHgTe were broad and had low intensity. However, after the annealing process (Figure 5), the intensity of CdHgTe peaks increased, and the peaks became more distinct. This trend was also observed in other samples grown at different deposition potentials. This suggests that annealing enhances the crystalline quality of the films, likely due to the relaxation of stored elastic strain energy associated with lattice mismatches.

Upon comparing both patterns, it is evident that even after annealing, the crystal structure remains cubic (fcc). The crystal orientation also remains unchanged, as the dominant peak remains at (111). However, when the annealing temperature exceeds 300°C, patches start to appear in the films, indicating a decrease in film quality. The thickness of both types of films was measured, revealing a decrease in film thickness because of annealing.

Deposition Potential 'E'	**Hg content from EDAX**
$-500\ mV$	0.08
$-600\ mV$	0.043
$-700\ mV$	0.027

Table 1. EDAX composition data for HgCdTe thin films for composition X = 0.2

Energy Dispersive Analysis of X-rays (EDAX) was employed to investigate the composition of the CdHgTe films. EDAX analysis of all the films confirmed the presence of Cd, Hg, and Te ions. The Cd:Hg ratios are summarized in Table 1 for the films grown from a bath composition of X=0.2 at deposition potentials of -500 mV, -600 mV, and -700 mV.

The results indicate that the Hg content in the films is 0.08, 0.043, and 0.027, respectively. This suggests that, for a consistent bath composition, the composition gradually shifts from being Hg-rich to Cd-rich within the plateau region as the potential is adjusted from left to right. The range of the compositional ratio Hg/Cd in the deposit is influenced by the ionic makeup of the bath. Elevating the Hg/Cd ionic ratio of the bath leads to an increase in the maximum value of the corresponding ratio within the deposited films.

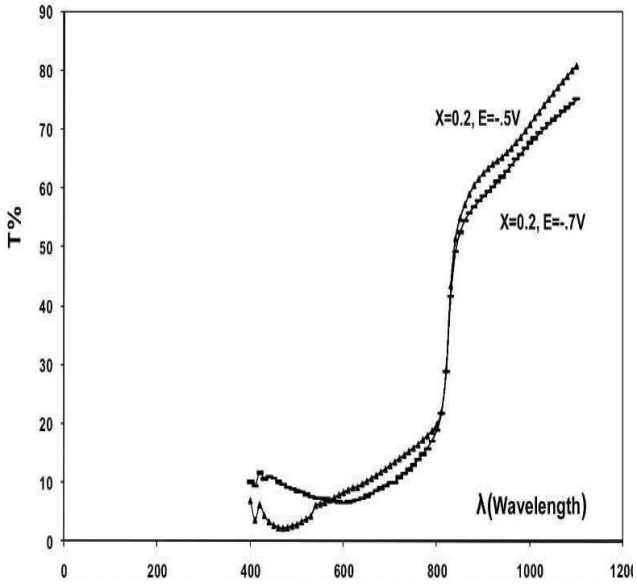

Fig. 6 Transmission spectra for films grown at deposition potentials of -500 mV and -700 mV w.r.t. SC electrode grown from the bath of composition X = 0.2

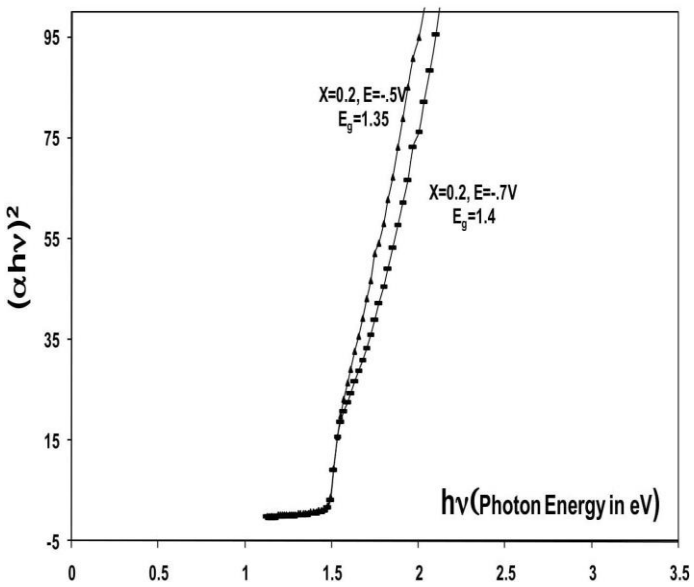

Fig. 7 Photon energy $h\nu$(eV) versus $(\alpha h\nu)^2$ plots of the films grown at deposition potentials of -500 mV and -700 mV w.r.t. SC electrode grown from the bath of composition X = 0.2

In addition to X-ray diffraction and EDAX studies, optical analysis is among the crucial techniques for characterizing materials. The optical transmission spectra of the films were examined to determine the spectral characteristics of optical absorption as well as the nature and magnitude of the bandgap. Figures 6 and 7 illustrate the transmission spectra and plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$, respectively, for films with a bath composition of 0.2 grown at deposition potentials of -500 mV and -700 mV. Throughout the analysis, the reflection coefficient was assumed to remain constant at 20% for all wavelengths. The direct bandgap values for the samples were obtained from the linear intercepts of the $(\alpha h\upsilon)^2$ versus $h\upsilon$ plots.

Conclusions

EDAX and optical analyses carried out on as-grown films produced at varying deposition potentials from the electrochemical bath shows a decrease in the Hg content within the films as the potential is shifted towards more negative values within the plateau region of the cyclic voltammogram of the bath. X-ray diffraction (XRD) investigations indicate deterioration in film quality when the potential is shifted towards more negative values. However, this decrease in quality can be reversed without modifying the crystal structure or orientation by subjecting the films to annealing at 300°C in a rough vacuum (10^{-2} - 10^{-3} mm of Hg) for one hour after their growth.

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