

**CHARACTERIZATION OF CADMIUM ZINC TELLURIDE THIN FILMS
PREPARED BY MAGNETRON SPUTTERING FROM A SINGLE TARGET**

By

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ABSTRACT

CHARACTERIZATION OF CADMIUM ZINC TELLURIDE THIN FILMS
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In this thesis the structural, optical, material characterization of CdZnTe (CZT) thin films are performed under different temperatures. There is a significant difference here, which is the CZT thin films, as differently from the previous film techniques known in the literature, which are made using Radio Frequency (RF), and generated from CZT target material placed on a single RF sputterer instead of sputtering CdTe and Zn from two separate RF. $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin films were deposited subsequently onto heated and unheated glass front substrates by using a single sputtering target. 200 nm thin films were fabricated and characterized using UV– transmission spectroscopy, X-ray Diffraction

(XRD), X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive Spectroscopy (EDS) and Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM). The transmission spectra in the region of the optical absorption band edge were measured for as-deposited and heat-treated CdZnTe samples. Band gap of the deposited films were found to be in the ranges of 1.70-2.24 eV. The XRD studies revealed that heated $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films have a cubic-oriented (111), (220) and (311) polycrystalline structure, whereas heated films are mostly-amorphous. The effect of annealing temperatures on the composition of the thin films were then discussed. XPS measurements were performed in the depth profiling mode in order to understand the chemical composition of the films. SEM images were used for producing a magnified image of the sample and it was observed that post-annealing and deposition temperature has an explicated effect on the modification of the CdZnTe thin film structure and morphology. The chemical composition of source and deposited CdZnTe thin films were investigated by using energy dispersive X-ray analysis (EDX or EDS) measurements. AFM was used for imaging CdZnTe thin films which deposited under different radio Frequency sputtering temperature and annealing temperature, then these images were analyzed with high-resolution. Finally, the concurrency between the bandgap values which were calculated from all of the other analysis methods and the UV spectroscopy method were examined.

Key Words: CdZnTe, SEM, AFM, XRD, EDX, XPS, deposited, material, optical, and structural analysis.

ÖZET

PÜSKÜRTME YÖNTEMİYLE TEK TARGETTAN BÜYÜTÜLEN
KADMİNYUM ÇİNKO TELERYUM İNCE FİLMİNİN KARAKTERİZASYONU

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Bu tezde CdZnTe ince filmlerinin yapısal karakterizasyonu optik karakterizasyonu ve özdeksel karakterizasyonu değişik sıcaklıklarda incelenmiştir. Burada, literatürde daha önce bilinen, RF kullanılarak elde edilen ve CdTe ve Zn'nin iki ayrı RF'den püskürtülmesi yerine tek bir RF püskürteci üzerine yerleştirilmiş CZT hedef maddesinden elde edilen film tekniklerinden farklı olarak uygulanmış; çok önemli bir fark bulunmaktadır. $Cd_{1-x}Zn_xTe$ ince filmleri tek bir püskürteç hedef kullanılarak sırasıyla ısıtılmış ve ısıtılmamış cam kaplama ana malzemesi üzerine çökeltildi. UV yayılım spektroskopisi, X-ışınlarının kırınımı (XRD), X-ışınlarının foto elektron spektroskopisi (XPS),

enerji dağınımlı X-ışınları spektroskopisi (EDS) ve Atomik kuvvet mikroskobu(AFM) ve Tarayıcı electron mikroskopisi (SEM) kullanılarak 200nm'lik ince filmler üretilmiş ve bunların özellikleri belirlenmiştir. Optik emilim kuşak kenarı bölgesindeki aktarım spektraları çökeltilmiş olan ve ısı verilmiş CdZnTe örnekleri üzerinden ölçülmüştür. Çökeltilen filmlerdeki bant aralığının 1.70 ila 2.24 eV arasında değiştiği görülmüştür. XRD araştırmaları, ısıtılan filmlerin çoğunlukla amorf olmasına karşın ısıtılan $Cd_{1-x}Zn_xTe$ filmlerinin izometrik -küp şekilli (111) ve polikristal yapılı (220) ve (311) olduğunu göstermiştir. Daha sonra tavlama sıcaklığının ince filmlerin bileşimi üzerindeki etkisi üzerine tartışılmıştır. XPS ölçümleri, filmlerin bileşimini öğrenmek amacıyla derinlik görüntü modunda gerçekleştirilmiştir. SEM görüntüleri, örneğin büyütülmüş bir görüntüsünü üretmek için kullanıldı ve kaplama ve fırınlama sıcaklıklarının CdZnTe ince filmlerinin morfolojik ve yapısal özellikleri üzerinde değişikliğe neden olduğu gözlemlendi. Kaplanmış CdZnTe ince filmleri ve kaynağın kimyasal bileşimleri, enerji yayılımı X-ray analizi (EDX veya EDS) ölçümlerini kullanarak incelendi. AFM, çeşitli radyo frekansı saçılım sıcaklıkları ile çeşitli fırınlama sıcaklıkları altında kaplanan CdZnTe ince filmlerinin görüntülenmesi için kullanıldı. Daha sonra bu görüntüler yüksek çözünürlükte analiz edildi. Son olarak, UV spektroskopisi yardımıyla bulunan bant aralığı değerleri ile tüm diğer analiz metotlarından yararlanılarak hesaplanan bant aralığı değerlerinin uyumluluğu irdelendi.

Anahtar kelimeler: XRD, SEM, AFM, EDS, XPS, CdZnTe, kaplama, özdeksel, optik ve yapısal analiz.

To my Grandfamily....



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CHAPTER 1

INTRODUCTION

Cadmium Zinc Telluride (CZT) which is the ternary II – VI compound has been used in order to substrate the infrared applications for many years. At the same time, CZT ternary semiconductors have been an important area of usage and they will attract more interest because of their wide applications [1-5]. CZT is a very important semiconductor material and used in Solar cells, Electro optical modulators, X-ray and Gamma ray detectors, and other Optoelectronic devices. The properties of CZT make it a primary compound for terrestrial photovoltaic applications [6,7]. Various methods have been used to create $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films: molecular beam epitaxy [8], liquid phase epitaxy [9], electro deposition [10], close space vapour transport [11], laser ablation [12], thermal vapour evaporation [13-16], metal–organic chemical vapour deposition (MOCVD) [17] and sputtering [18]. The last method has been considered as a flexible process, suitable for the fabrication of both multilayer solar cells and photo detectors. As it is known, there are many papers experimentally studied a wide range of compositions of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films on glass, but these films were produced by using a few sputtering targets, like CdTe target and Zn powders or CdTe and ZnTe targets [19]. Therefore, investigating the structure of single target sputtered $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films on glass for the entire range of $0 < x < 1$ needs a significant scientific interest. Another important question is how the structural stability of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ is specified.

The ternary system Cd–Zn–Te equilibrium phase diagram has been determined by X-ray diffraction (XRD) methods [20, 21]. XPS depth profile spectra were measured after removing the surface layer of the sample by argon ion etching.

The band gap of CZT is adjustable from the visible to infrared amount of electromagnetic spectrum; therefore CZT layers can be implemented without hesitation as optoelectronic devices. Two tandem solar cells whose efficiencies are greater than 20% include two single junction solar cells that have different band gaps. There are two types of planes (111), one of them is formed by casual distributed Cd and Zn atoms and the other formed by Te atoms [22]. It is very important to fabricate $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ alloy with the required lattice parameter. These lattice parameters of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ depend on Zn concentration. x is the amount of Zn concentration in the compound. $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ has been deposited by Sputtering, Molecular Beam Epitaxial, etc. for solar cell applications [23].

CZT also has several properties that make it highly requested for desire applications, such as spectroscopy. Its high detection efficiency, high resolution, low cost, and good signal to noise ratio at room temperature make it a product of choice for many applications. The most important parameter to make radiation detector is the band gap. Band gap depends on the Zn concentration in the compound. The bandgap changes by only a few meV by varying zinc concentration with a few percentage which is significant for idea of the most detector related parameters. Generally the ratio of Zn with respect to Cd in a typical CZT body is less than 10% [24].

1.1.2 Zinc Telluride:

ZnTe has a wide band gap of 2.4 eV with a dielectric constant of 8.7. It is commonly used in solar cells, gamma ray detectors, and waveguide modulators and IR optics. At the same time, ZnTe rubedinous crystalline has two solid structures, especially hexagonal and Zinc blonde structure. Nitrogen doped ZnTe produced by sputtering can be used as a back contact for ZnTe solar cells. The efficiencies with ZnTe for back contact on ZnTe solar cells have reached to 10-11% percent.

1.1.3 Cadmium Telluride:

Cadmium Telluride is composed of a Cd atom which is tetrahedrally surrounded by four Te atoms. The band gap of semiconductors theoretically must be 1.5 eV for ideal solar cells applications. The band gap of CdTe is near optimum 1.45 eV, therefore CdTe is a promising material for high efficiency thin film solar cell. CdTe can be deposited by different techniques, such as; thermal vapour evaporation [13-16], metal–organic chemical vapour deposition (MOCVD) [17] and sputtering [18]. The efficiency reported in thin films of CdTe Grown by sputtering is 15% [25].

1.2. Previous Studies

In recent years, the research and study of on the thin films CZT alloys have enormously increased because of CZT's important industrial applications, which are solar cell, photo detectors, X-ray detector, gamma ray detectors and optoelectronic devices, [26-27] , CZT thin film has suitable band gap to be used in solar cell technology because of its tunable bandgap (between 1,5-2,25eV) [28]. The band gap of top cell should be in the range of 1.5—1.8 eV for high efficiency[29]. The subject

studied by many recent papers has been focused on the optical properties of amorphous semiconductors. The optical amorphous of semiconductors depends exceedingly on the composition of the compound [30-31]. The optical properties of materials are related to their electronic band structure, atomic and electrical structure.

The high x value in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystal was developed for the first time by Doty et al. [32] in 1993. The following characteristics were obtained; 1-high band gap energy, 2- high atomic number, 3-good mechanical strength, 4- high resistivity, 5-photosensitivity, 6-relatively good charge transport qualities are the progress crystal [33]. $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ X-ray and gamma ray detectors have a lot of advantages than the other detectors. Başol et al. [34] He has equipped CZT film by annealing the piled up elemental layers of Cd, Te and Zn. The elemental layers were deposited by exploiting bindings of Electrodeposition and thermal evaporation followed by annealing. A shift in (111) reflection and linear variation of the lattice parameter with composition appeared figuration of CZT compound. [35]. Dhere et.al.[36] He obtained that when deposited by sublimation from a mixed powder source, it is very difficult to retain much Zn in the film. Bansal and Rajarman et.al.[37] Thin films of CZT's have been deposited from aqueous solution on substrate. On the other hand, the deviation of Zn and Te ions is less soluble in aqueous medium can cause difficulty in controlling the stoichiometry of semiconductor thin films. Chaure et.al.[38] $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$'s application electrodeposited using non aqueous bath photovoltaic application is reported.

The $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ where $0 < x < 1$ thin films with blende type structure has many applications because of its several properties; for instance, the tunability of band gap

and lattice parameter with alloy composition, high amount of optical transmittance below the band gap and high optical absorption coefficient above the bandgap. These properties of CZT ternary semiconductor material have been interested by many scientists [39-44].

1.3. Motivation and Present Studies:

In the present study the structural, optical, electrical and material properties of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ are examined. The improvement of semi-insulating CdTe and CZT have been testified after more than 40 years of laboratory exploration. Following that at room temperature semiconductor detector technology has many applications such as especially industrial monitoring, medical and industrial imaging, calibration, nuclear safeguards, transportation safety and security.

This thesis consists of four main chapters. In the chapter one, structure of CZT thin films has been introduced. In the chapter two, the theoretical background of deposition techniques of CZT thin films, thin film structure, and characterization techniques have been introduced. In the chapter three, the experimental techniques and detailed explanation of measurement systems, main stages of characterization of CZT thin films using RF magnetron sputtering techniques for deposition are given. In addition, the X-ray diffraction (XRD), Energy Dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) are used for characterizing of CZT thin films. Final chapter touches upon the results obtained for the deposited thin films as a conclusion of conducted several type of structural, optical characterization measurements and material characterization measurements.

CHAPTER 2

THEORITICALLY CONSIDERATIONS

2.1. The main reason behind of the CZT thin films

Cadmium zinc telluride (CZT) semiconductor detectors have suitable band gap (between 1.45 and 2.20 eV) energy due to their atomic number value which is Cd:48, Zn:30, Te:52 and can be used at room temperature. Therefore, their photon detection efficiency is better than that of Silicon or Germanium and CdTe (Cadmium Telluride). Although CZT can be used at room temperature however it has a disadvantage operating at the temperatures above 400⁰C.

CZT detector has high efficiency and good energy resolution if only the incident photon energy is less than a few hundred keV because the photon interaction with exists near the detector surface that the charge collection efficiency is high. The charge collection efficiency becomes low due to the hole trapping phenomena whereas the photon interaction occurs at accidental locations in the detector and the incident photon energy is over a few hundred keV [45].

2.2. Thin film structure

The thin-film and multi-layered coatings are largely used in material science, X-ray optics, microelectronics and optics. The quality of thin film is the primary factor for definition parameters of microelectronic and optical devices. Thin films

can be characterized with many different ways. The most common thin films properties and their related measurement techniques are given below:

- **Thickness** (spectrometer, ellipsometer, step height, Electron microscope, Rutherford Backscattering (RBS), quartz crystal monitor),
- **Optical properties** : refractive index, extinction coefficient, transmission, reflection, absorption (spectrophotometer, ellipsometer),
- **Electrical conduction** (4 point probe, eddy current) ,
- **Crystal structure** (TEM, XRD),
- **Microstructure** (SEM),
- **Chemical/Elemental Composition** (AES, XPS, EDAX, SIMS) ,
- **Thin film stress** (Curvature of coated sample),
- **Thin film adhesion** (Tape test, pull tester) [46] .

2.3. Deposition Techniques

2.3.1. Chemical Vapor Deposition (CVD)

Chemical vapor deposition is also known as metalorganic chemical vapor deposition (MOCVD), is a chemical process used to generate high-purity, high-performance solid materials. The process is often used in the semiconductor industry for producing thin films. In a characteristically CVD process, the wafer (substrate) is subordinated to one or more volatile precursors, which react and decompose on the substrate surface to produce the desired deposit. Frequently, volatile products are also produced, which are removed by gas flow through the reaction chamber. Micro fabrication processes widely use CVD to deposit materials in various forms,

including monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include silicon, carbon fiber, filaments, carbon nanotubes, SiO₂, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride, titanium nitride, and various high-k dielectrics. The CVD process is also used to produce synthetic diamonds [47].

2.3.2. Sputtering

Sputter deposition is a method to deposit thin films by sputtering onto a "substrate" [48]. Sputtered atoms ejected into the gas phase are not in their thermodynamic equilibrium state, and tend to deposit on all surfaces in the vacuum chamber. A substrate (such as a wafer) placed in the chamber will be coated with a thin film. Sputtering techniques usually use argon plasma. Because of the low substrate temperatures used, sputtering is an ideal method to deposit contact metals for thin-film transistors. Perhaps, the most familiar products of sputtering are low-emissivity coatings on glass, used in double-pane window assemblies. The coating is a multilayer containing silver and metal oxides such as zinc oxide, tin oxide, or titanium dioxide. Sputtering is also used as the process to deposit the metal (Aluminum) layer during the fabrication of CD and DVD discs [49].

2.3.3. Laser Ablation

The process which is used to remove material from a solid or liquid surface by irradiating it with a laser beam is called laser ablation. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates. At high laser flux, the material is typically turned into plasma, laser ablation usually refers to

removing material with a pulsed laser, but the material can be ablated with a continuous wave laser beam if the laser intensity is high enough. Laser pulses can vary over a very wide range of duration (milliseconds to femtoseconds) and fluxes, and can be precisely controlled. This makes laser ablation very valuable for both research and industrial applications [50].

2.3.4. Liquid Phase Epitaxy:

Liquid phase epitaxy (LPE) is a method to grow semiconductor crystal layers from the melt on solid substrates. This happens at temperatures well below the melting point of the deposited semiconductor. The semiconductor is dissolved in the melt of another material. At conditions that are close to the equilibrium between dissolution and deposition, the deposition of the semiconductor crystal on the substrate is slow and uniform. Typical deposition rates for monocrystalline films range from 0.1 to 1 $\mu\text{m}/\text{minute}$. The equilibrium conditions depend very much on the temperature and on the concentration of the dissolved semiconductor in the melt. The growth of the layer from the liquid phase can be controlled by a forced cooling of the melt. Impurity introduction can be strongly reduced. Doping can be achieved by the addition of dopants. This method is mainly used for the growth of compound semiconductors. Very thin, uniform and high quality layers can be produced [51].

2.3.5. Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE) is one of the several methods for depositing single crystals and multilayers. It was invented in the late 1960s by J.R. Arthur and Alfred Y. Cho at Bell Telephone Laboratories. Molecular beam epitaxy takes place in high vacuum (10^{-8} pa). The slow deposition rate (typically less than 1000 nm per

hour), which allows the films to grow epitaxial is the most important aspect of MBE. The slow deposition rates require proportionally better vacuum to achieve the same impurity levels as other deposition techniques [52].

2.3.6. Electrodeposition

This process is also known as "electroplating" and is typically restricted to electrically conductive materials. There are basically two technologies for plating: Electroplating and Electroless plating. In the electroplating process the substrate is placed in a liquid solution (electrolyte). When an electrical potential is applied between a conducting area on the substrate and a counter electrode (usually platinum) in the liquid, a chemical redox process takes place which results in the formation of a layer of material on the substrate and usually some gas generation at the counter electrode. In the Electroless plating process, a more complex chemical solution is used, in which deposition happens spontaneously on any surface which forms a sufficiently high electrochemical potential with the solution. This process is desirable since it does not require any external electrical potential and contact to the substrate during processing. Unfortunately, it is also more difficult to control with regards to film thickness and uniformity. The Electrodeposition process is well suited to make films of metals such as copper, gold and nickel. The films can be made in any thickness from $\sim 1\mu\text{m}$ to $>100\mu\text{m}$. The deposition is best controlled when used with an external electrical potential, however, it requires electrical contact to the substrate when immersed in the liquid bath. In any process, the surface of the substrate must have an electrically conducting coating before the deposition can be done.

2.4. Cadmium Zinc Telluride and its Deposition

Sputtering is used comprehensively in the semiconductor industry, for depositing thin films of the various materials in integrating circuit processing. Sputtering is also an ideal method for depositing contact metal for thin film transistor on account of the low substrate temperatures used. There are some advantages of using the sputtering as a deposition technique; one of them is that the deposited films have the same composition as the source material. When using RF sputtering charge build up on insulating targets can be get out where the sign of anode-cathode bias voltage is changed at high rate. RF sputtering works is good method for producing highly insulating oxide films however only with the added expense of RF power supplies resistivity matching networks.

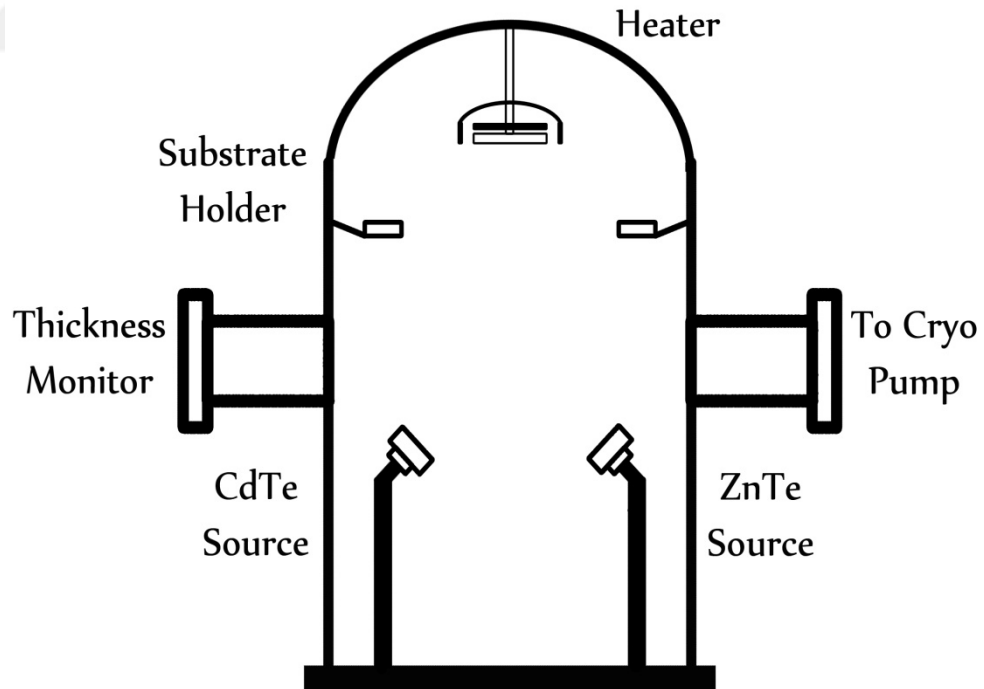


Figure2.1. Co-sputtering chamber for CZT deposition

The sputtering technique submits in principle a simple and flexible control of the film stoichiometry round a large scale at sort of low cost, and also using a high value for industrial applications [53]. Figure 2.1 shows the schematic representation of a sputtering system.

2.5. Material Characterization Techniques

2.5.1. Surface Analysis Methods.

Surface analysis technique is used to measure microscopic features from microstructures to nano-scale dimensions. Surface material analysis contains micro structural characterization of material including polymers, films, coatings, geological and mineral samples, pharmaceuticals, raw materials, metals, plastics, ceramics, glass, food, dust, contaminants and other sample types. Surface analysis includes analysis of particle and its identification as an example the structural analysis semiconductor detection of identification of physical and chemical deficiency.

Surface and Microstructure analysis techniques:

- ❖ **SEM** (Scanning Electron microscopy) *,
- ❖ **TEM** (Transmission Electron Microscopy),
- ❖ **EDXA** (Energy Dispersive X-ray) *,
- ❖ **SPM** (Scanning Probe Microscopy),
- ❖ **AES** (Auger Electron Microscopy),
- ❖ **XRD** (X-ray Electron Microscopy) *,
- ❖ **AFM** (Atomic Force Microscopy) *,
- ❖ **XPS** (X-ray Photoelectron Spectroscopy) *,

- ❖ Image Analysis,
- ❖ Optical Light Microscopy,
- ❖ Nano-Materials Analysis and Research,
- ❖ Cryo EM Microscopy,
- ❖ SSIMS Static Secondary Ion Mass Spectrometry (Surface- SIMS),
- ❖ Vertical Scanning, Phase Shifting Interferometer [54].

2.5.1.1.X-ray Photoelectron Spectroscopy (XPS)

XPS was developed in the mid 1960s by K. Siegbahn and his groups. In 1981 he won the Nobel Prize for Physics for his work in XPS. The phenomenon was installed on the photoelectric effect which summarized by Einstein in 1905. Where the concept of the photon was used to identify eliminating of electrons from a surface When the photons crash upon it [55]. Figure 2.2 shows schematic diagram of XPS system.

An XPS spectrum of a sample involves information about the elements available, their chemical state and their distribution. All of this parameters can be obtained from a spectrum fundamentally but the certainty of quantification trusts largely to the method of spectral analysis. The spectrum has to be unstitched in its components before quantification if peaks originating from types in a sample add on. The common procedure contains subtraction of a Shirley-type background from the overall spectrum and posterior fitting of the resulting background corrected spectrum with a set of peaks [56].

*They were used in this study.

While XPS is a surface sensitive technique, a depth profile of the sample in terms of XPS quantities can be obtained by combining a sequence of ion gun etch cycles interleaved with XPS measurements from the current surface. An ion gun is used to etch the material for a period of time before being turned off whilst XPS spectra are acquired. Each ion gun etch cycle exposes a new surface and the XPS spectra provide the means of analyzing the composition of these surfaces.

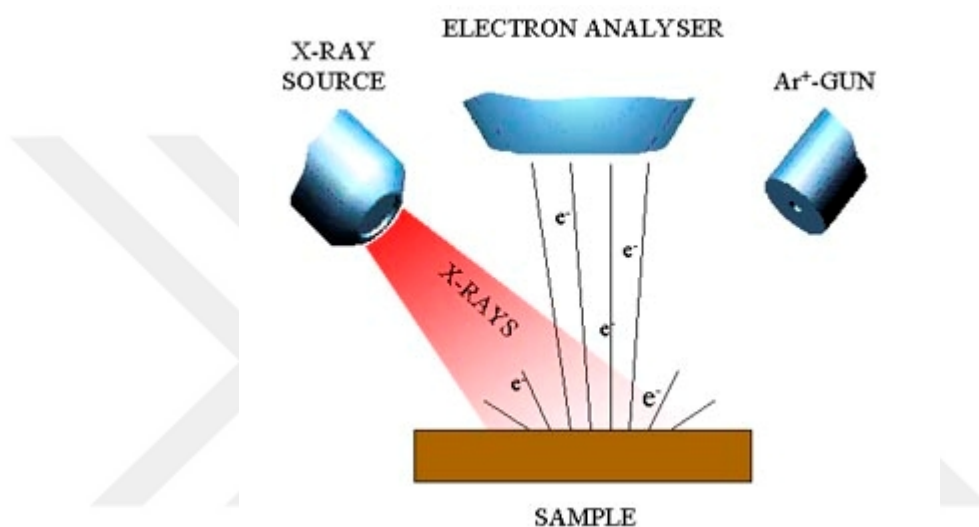


Figure 2 . 2. Schematic diagram of XPS system [57].

2.5.1.2. Energy-Dispersive X-ray Spectroscopy (EDX- EDS)

EDX is usually used on a Scanning Electron Microscope (SEM) and can be used to determine chemical composition for regions as small as $0.1\mu\text{m}$ at low voltage, even smaller for elements of high atomic number. The depth of analysis also can be as little as $0.1\mu\text{m}$ or, again, much less for elements of high atomic number. These two parameters are functions of the beam voltage and the sample composition. In this process, the sample is bombarded with a beam of electrons [58]. EDX or EDS

is on the basis of the collection and energy dispersion of characteristic X rays. When X rays are ionized by a high radiation, the atoms in a material emit characteristic X rays. The elements in an EDX unit are the mother of high energy radiation, a solid state detector and signal processing electronics. The resulting from X ray spectrum concludes a series of peaks. These peaks represent the type and relative amount of each element in the sample [59]. EDS System is shown in figure 2.3. which include a sensitive X-ray detector, a liquid nitrogen for cooling, and analyse energy spectra.

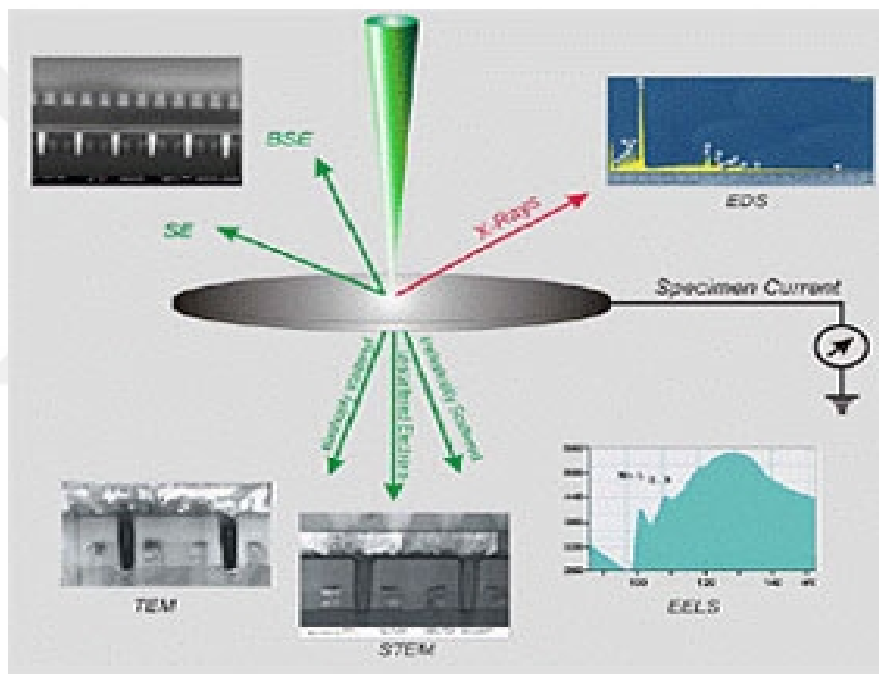


Figure 2.3. Schematic diagram of EDX-EDS system[60]

2.5.1.3. Scanning Electron microscopy (SEM)

Scanning electron microscopy (SEM) developed in the early 1950's which have invented new areas of study in the medical and physical examination. SEM is used in order to analyze the surface of materials it also measures and evaluates surface fitting, deposits, contaminants, particles, filter residues, characterization of

dust, failure analysis and other applications. SEM is a microscope which uses electron instead of light to form an image.

There are many advantages of using the SEM over traditional microscope (light microscope). Some of them are; the SEM has a large depth of field, which allows more specimens to be in focus at one time. Also it has much higher resolution because of those closely spaced specimens that can be Grown at much higher levels.

2.5.1.4. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was invented in 1980s and since this date, it has come to be used in all fields of science as example chemistry, physics, material science, nanotechnology, astronomy biology medicine and more. AFM is very interesting technique that measure surface structure with high resolution and accuracy. An atomic force microscope allows, for example, to get images showing the arrangement of individual atoms in a sample, or to see the structure of individual molecules. Very small images only 5 nm in size, showing only 40–50 individual atoms, can be collected to measure the Crystallographic structure of materials, or images of 100 micrometers or larger can be measured, showing the shapes of dozens of living cells at the same time [61-65]. Furthermore, as well as its use as a microscope, which is to say as an imaging tool, AFM has various ‘spectroscopic’ modes, that measure other properties of the sample at the nanometer scale. An AFM is different from other microscopes which are image by focusing light or electrons onto a surface, like an optical or electron microscope. It physically feels the sample’s surface with a sharp probe and creating a map height of the sample’s surface. AFM has some advantages from other microscopes which are 1-) It generates true, three-

dimensional surface images; 2-) it does not require special sample treatments that can result in the sample's destruction or alteration; and 3-) it does not require a vacuum environment in order to operate. Figure 2.4. shows the schematic diagram of Atomic Force Microscopy.

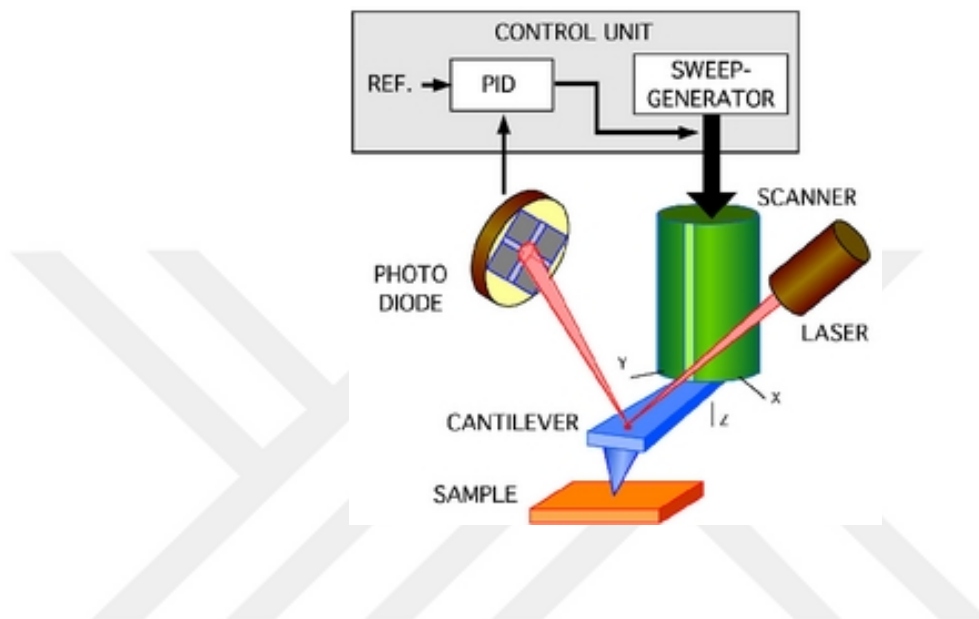


Figure 2.4. Atomic Force Microscopy (AFM)[66]

2.5.2. Structural characterization

Several analytical techniques such as X-ray diffraction, neutron diffraction analysis, electron microscopy and electron diffraction are used for fixing of structural features of solid state materials. With the help of these techniques lattice parameters can be calculated, the phases existing in the structure can be identified, crystalline state can be brought (crystalline, polycrystalline or amorphous), and also defects can be detected. For determining these parameters we used X-ray diffraction technique [67].

2.5.2.1. X-ray Diffraction Technique

X-rays are electromagnetic radiation of wavelength near $1 \text{ \AA}$ (10^{-10}m) which is about the same size as an atom. And also X-rays are the electromagnetic waves owning energies ranging from 200eV- to 1MeV. By the time interacting with a solid state material in several ways these are; absorbed, emitted, reflected, or transmitted used for identifying of structural parameters.

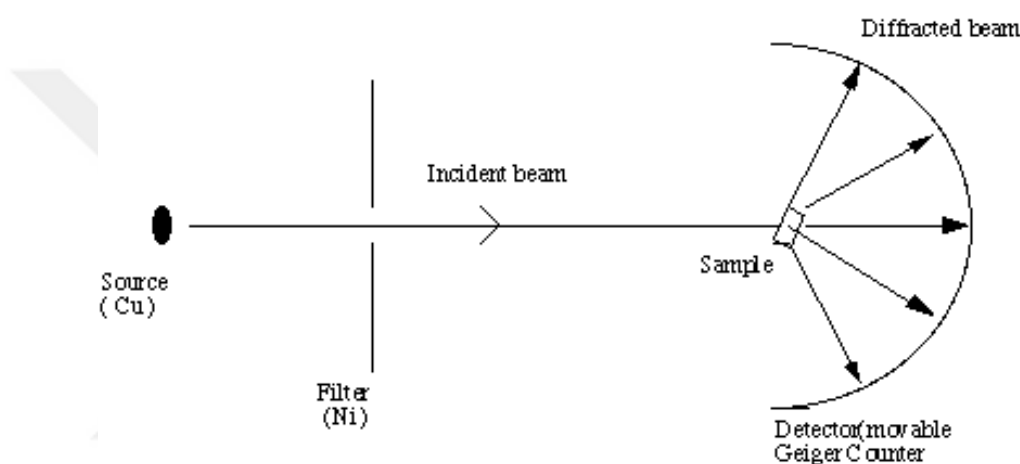


Figure 2.5. Schematic of an X-ray powder diffractometer.[68].

Schematic of an X-ray powder diffractometer is shown in figure 2.4. As it is seen from the Fig.2.5, the most commonly used copper for emitting the X-ray radiation. Diffraction occurs in all of possible orientation of 2θ when the incident beam strikes a powder sample. A moveable detector as an example a Geiger counter, which is connected to a chart recorder uses for detecting the diffracted beam.

A diffraction model can be established when X-rays interacts with a material having an ordered structure. This model gives important information about the structure of a material and it can be taken as the fingerprint of a substance. If incident of X-rays are on a crystalline substance, a constructive interference is taking place in

specific orientations and ends up with generation of well defined X-ray diffraction patterns [69]. The crystal plane or the orientation of a surface be able to defined by taking into account how parallel plane intersects the main crystallographic axes of solid [70]. Miller indices which represent with h , k , l , are the orientation and inter distances of parallel planes. Here h , k , l means three dimensional h , is a -axis, k , is b -axis, l is c -axis. a , b , and c (length) and α , β , and γ angles between a , b , and c are lattice constants or parameters that can be defined by X-ray diffraction[71]. A unit cell can be declared the smallest volume element repetition in three dimensions that may construct all the structure. Many unit cells are represented with different shapes. Seven unit cell shapes meet with this requirement and named as seven crystal systems [72] which, are shown in table 1.

Table1: Inter planar spacing d_{hkl} for different crystal systems and their dependency on Miller indices hkl . Parameters a , b and c give the lengths of the crystallographic unit cell, while α , β and γ specify the angles between them [73]

System	Crystal system	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a=b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma \neq 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$

d_{hkl} is the distance between two adjacent planes and defined by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

Equation 1 can be using for specific crystalline structure.

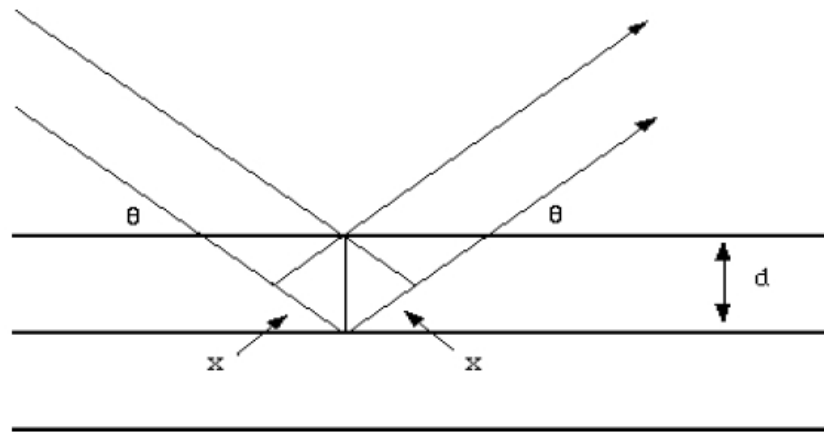


Figure 2 . 6. Diffraction of X-rays from parallel planes.

From the figure 2.5, the diffraction of X-rays from the parallel planes can be determined. And also it can be determined the size and the shape of the unit cell for any compound most easily while using the diffraction of X-rays.

There are several conditions that can be responded from diffraction after incident. One of these conditions is the angle between the incident beams. Reflecting planes ought to be equal to that of diffracted beam and reflecting planes. The other condition is about the incident and reflected waves from planes ought to be in phase and the difference in path length must be an integral number of wavelengths. From these conditions, Bragg's law is derived:

$$n\lambda = 2d \sin(\theta) \quad (2)$$

Where n , λ , d , and θ are the order of diffracted beam, wavelength of the incident X-ray, inter-planar spacing of parallel planes, and Bragg's angle, respectively. Figure 2.6. shows an A powder X-ray diffractometer schematically.

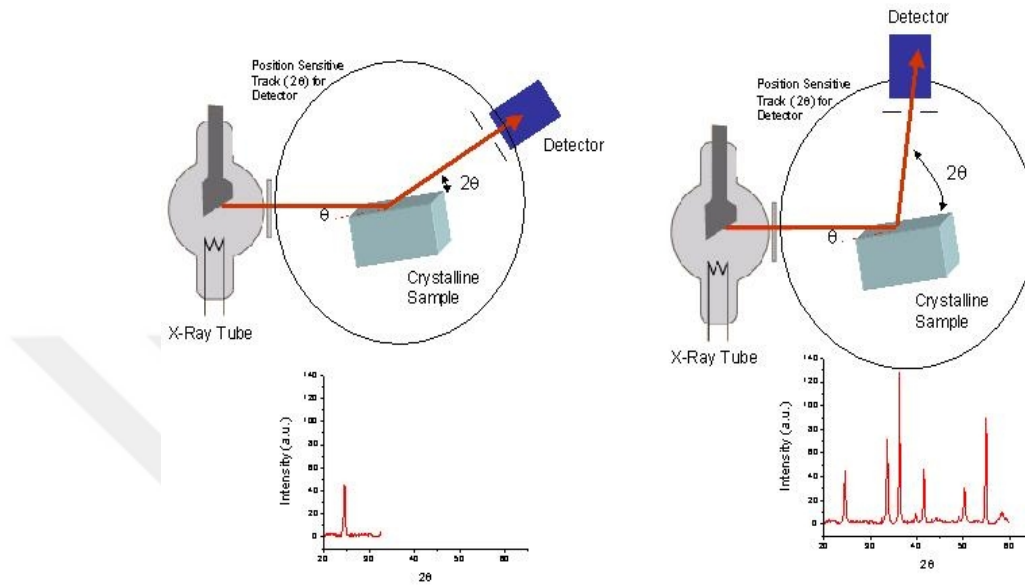


Figure 2.7. A powder X-ray diffractometer [74].

2.6. Optical Characterization

Semiconductors can be involved in an interaction with light in some ways and result in editing of different process as an example reflection, transmission, absorption, and scattering. For identifying the optical properties of semiconductors many optical instruments are designed. Thin film deposition process is the example of the suitable characterization during production process which is allowed by contactless and non-destructive optical characterization techniques [75]. The basic optical characterization techniques are optical microscopy, optical absorption, photoluminescence, Raman spectroscopy, and optical modulation techniques.

2.6.1. Optical Absorption and Transmission

For determining the band structure of materials optical absorption and transmission are the best measurement techniques. The absorption which is defined as the energy loss occurring as a result of interaction of the electrical charges inside a material with the electromagnetic waves dropped onto the material is used by the atoms of the material. When any material with t thickness interacts with an electromagnetic wave, at the absorption is given as follows.

$$I = I_0 e^{-\alpha x} \quad (3)$$

I is the intensity of electromagnetic wave which passed t thickness material. I_0 is the intensity of electromagnetic wave which sending on the sample, α is the absorption constant, x is thickness of sample

Absorption coefficient α depends on the wavelength of the electromagnetic wave, density of the material and the forbidden energy range of the material, and is found by the following equations.

$$A = \log_{10}(I_0/I) \quad (4)$$

$$\alpha = 2.303 \frac{A}{t} \quad (5)$$

Where A is the absorbance dependence on the α (absorption constant), wavelength of the electromagnetic wave, density of material and band gap of the material. The most useful method for researching the band structure of semiconductor is the optical absorption method. The information about band type and forbidden energy range can be found by this method [76].

The absorption process might be fulfilled with some mechanisms; these are band to band, intercondition band, intervalence band, donor to conduction band,

acceptor to conduction band, valence to donor, acceptor to conduction band, and donor to acceptor transitions that contribute to the total absorption coefficient. A photon motivates an electron from the valence band to the conduction band in the fundamental absorption process. In this process, both momentum and energy are conserved. By the time the minimum of the conduction band and the maximum of the valence band happen at the same value of the wave vector k , transitions are direct, and the material is referred to as a direct gap semiconductor. At the same time when the minimum of the conduction band and the maximum of the valence band happen at the different value of the wave vector k , transitions are indirect and the material is referred to as indirect –gap semiconductor. Figure 2.9 shows the schematic diagram of the direct and indirect bandgap of semiconductor.

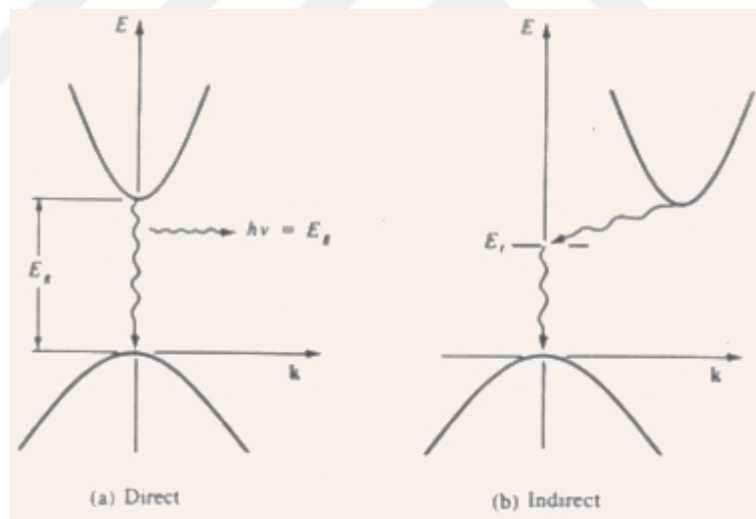


Figure 2.8. (a) direct band gap and (b) refers to indirect bandgap. [77]

The following formula shows how the absorption coefficient (α) can be calculated through the transmission (T) and reflection (R).[75]

$$T = \frac{(1 - R)^2 \exp(-ad)}{1 - R^2 \exp(-2ad)}$$

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1. Deposition Thin Films of CZT

3.1.1. Deposition of CZT Thin Films by RF Sputtering

The thin-film and multi-layered coatings are largely used in, materials science, X-ray optics microelectronics and optics. In this Thesis, CZT thin films prepared by using RF Sputtering system technique. Sputtering technique is the best technique used for thin film deposition and etching process.

CZT films were prepared on glass substrates held, at 200, 300 and 400°C, by using a radio frequency (RF) sputtering system. The RF power used in the deposition process was 40 W. The final vacuum reached, was 5×10^{-3} Torr before the Argon introduction. The single CZT (99.99%) target with 4 inch diameter was used. Growth rates were kept at 0.3 Å/s during the deposition.

In this study, CZT thin films were prepared by using a three magnetron D.C./RF sputtering system shown in Figure. 3.1. Fig. 3.1 shows the system includes one RF and two D.C. magnetron heads cooled by water circulation, vacuum chamber, substrate holder, heating elements of substrate holder, RF generator with a Dressler VM100A match box for the generation of RF plasma, vacuum gauges, a shutter, rough and turbo molecular pump, and other required accessory components. RF magnetron sputtering system is given in details in the Appendix 1.

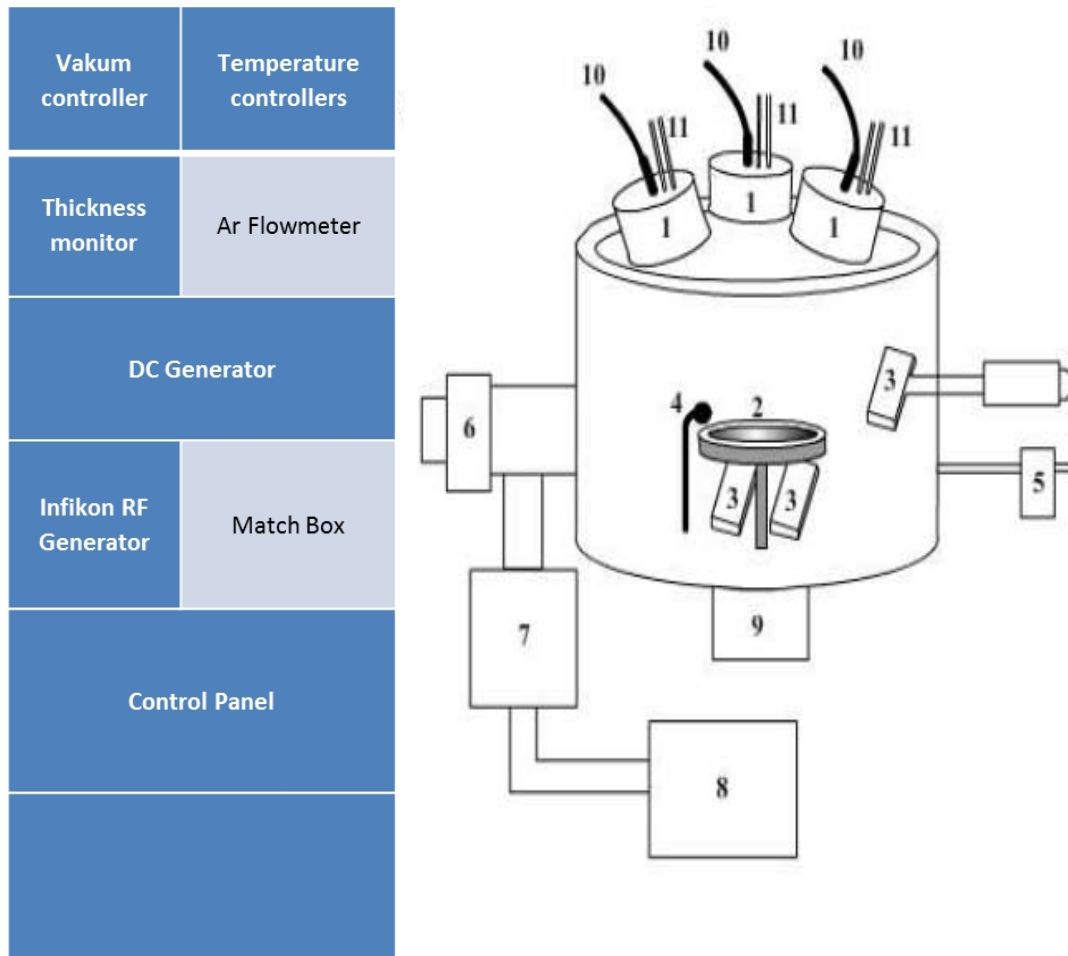


Figure 3.1: sputtering system used for deposition of CZT thin films. The devices of the sputtering system are: 1. Magnetron heads 2. Substrate stage 3. Heating elements (halogen lamps) 4. Thickness measuring crystal 5. Ar gas flow control unit 6. Vacuum valves 7. Turbo molecular pump 8. Roughing pump 9. Substrate holder rotating arrangement 10. RF/ DC magnetron connections 11. Water Cooling System 12. System control unit [78].

3.2. Heat Treatments

In this study were discussed the effect of RF Magnetron sputtering temperature which is the deposition temperature and annealing temperature on the

band gap of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin films. It was observed that the deposition temperature was affected on the layers as follows the x value.

3.2.1. Sputtering Temperature

CZT films were deposited on glass substrates, at 200, 300 and 400⁰C, in a radio frequency of (RF) sputtering system. Then the effect of temperature on the band gap was obtained.

3.2.2. Annealing

In this study as the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ Grown films show pure crystalline quality, all the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ samples were thermal annealed in a N_2 atmosphere at temperatures of 300 and 450 ⁰C, during 20 minutes. Higher values of temperature affect sensitively the thickness of the films. Measured film thicknesses were about 200 nm. The effect of the temperature on crystalline structure of the sample was observed (X-ray results).

3.3. Structural and Compositional Characterization of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$

3.3.1 X-ray Diffraction (XRD)

X-ray diffraction technique gives information about crystallographic chemical composition and physical properties of thin films. X-ray diffraction using for measuring the average spacing between layers , determining the orientation of a single crystal or grain, finding the crystal structure of an unknown material and measuring the size shape and internal stress of small crystalline regions.

In this study for investigating the structural properties of deposited CZT thin films a Rigaku Miniflex XRD system fitted with CuK α X ray source was used. XRD patterns were taken between 10- 60° angles with a speed 2° /min for all deposited thin films. XRD diffractograms obtained were compared with database including XRD patterns of known material structures supplied by JCPDS (Joint Committee on Powder Diffraction Standards) which maintains a database of powder diffraction patterns including the d-spacing(related to angle of diffraction) and relative intensities of observable diffraction peaks, supply a database consists of XRD spectra of organic and inorganic materials. Referring the analysis of XRD patterns precious knowledge about the structure of CZT thin films was obtained. The photo of X-ray diffraction system is shown is Appendix 2.

3.3.2.A. Energy Dispersive X-ray (EDX) Analysis Measurements

Energy-dispersive X-ray spectroscopy (EDS or EDX) which used for the elemental analysis or chemical characterization of a sample is an analytical technique. EDS –EDX is a microanalysis technique used for determining the composition of the sample. When the electron beam hits the sample X-ray are generated which have characteristic energies for each element. EDS-EDX can be conducted the micron to the nano-scale. Also, it can be mostly used as a property constituent of Scanning Electron microscopy (SEM). EDX accoutered SEM may obtain valuable information about the quantitative elemental analysis, sample surface morphology, and many other properties. Energy Dispersive X-ray spectroscopy system is given in details in Appendix 3.

3.3.2.B. Scanning Electron Microscopy (SEM) Analysis

SEM produces largely enlarged images by using electrons. A beam of electrons is produced by an electron gun from the top of the microscope. The electron beam that is held in a vacuum follows a vertical path through the microscope and it proceeds through lenses and electromagnetic fields. One time beam hits the sample, X-rays and electrons ejected from the sample. SEM system used is given in Appendix 4.

After the deposition the composition and the surface morphology of CZT thin films were researched exploiting a FEI quanta 400 FEG model SEM accoutered with EDX system in Central laboratory of Middle East Technical University.

3.3.4. C. Atomic Force Microscopy (AFM) Analysis

Atomic Force Microscopy (AFM) procures a number of advantages over conventional microscopy techniques. AFM can make measurements in three dimensions, x , y , and z (normal to the sample surface), thus enabling the presentation of three-dimensional images of a sample surface and also can probe the sample. This property of AFM provides a great advantage over any microscope. With good samples which are clean, with no excessively large surface features, resolution in the x - y plane ranges from 0.1 to 1.0 nm and in the z direction is 0.01 nm (atomic resolution). In this study used Atomic force microscopy which is in the central laboratory of METU for image and examines the CZT thin films.

3.3.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measures the elemental composition, experimental formula, chemical state and electronic state of elements

that exist within a material. XPS spectra obtained irradiation of a material with a beam of X-rays in spite of simultaneously measuring the number of electrons and kinetic energy from the top 1 to 10 nm of the material existence analyzed. The XPS system primarily consists of a high vacuum chamber, a lens system collecting the photo generated electrons and an X-ray source usually using $MgK\alpha$ a spectrometer containing electron energy analyzer and detector (1253,6 eV). XPS measurements for deposited CZT thin films executed by using UNISPECS ESCA system which is given in Appendix 5.

3.4. Optical Analysis

3.4.1. Absorption and Transmission Measurements

Optical properties of semiconductor study's basic characterization devices are the transmission and absorption. Optical absorption coefficient, optical bandgap, and optical constants especially refractive index and extinction coefficient can be calculated from transmission and absorption. Transmission and absorption can be measured with a photospectrometer which is an optic system.

In this study for the optical characterization, normal incidence reflectance R and transmittance T were determined in the wavelength range of 400–1100 nm using Shimadzu UV-360 spectrometer at room temperature. In the range of strong absorption of the radiation, the absorption coefficient has been calculated from the relation $\alpha = (1/d) \ln(100/T)$. A plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for the films of different composition is nearly linear indicating the direct bandgap nature of the films [79]. Extrapolation of the line to the $h\nu$ axis indicated a direct band gaps in the range 1.70-2.24 eV.

CHAPTER 4

RESULT AND DISCUSSION

This study deals with structural, electrical and optical characterization of CdZnTe with X-ray Diffraction, Atomic Force Microscopy (AFM) images, Energy Dispersive X-ray analysis, Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy measures. The effects of annealing temperature and the effects of Radio frequency (RF Sputtering) Sputtering temperature on the CdZnTe were investigated. The 200 nm thick CdZnTe thin films, differently from the film techniques known in the literature, made using RF, were deposited on glass CdZnTe using single CdZnTe target, instead of sputtering CdTe and Zn from two separate target.

4.1. CdZnTe Structural Properties

4.1.1. X-ray diffraction (XRD)

The typical diffraction patterns both for as-deposited and heat-treated $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin films at different temperatures are presented in Figure 4.1-4.4. It is observed that the deposition conditions play an important role in determining their structural characteristics. As the deposition temperature increases, the peak intensity also increases. The X-ray diffraction patterns of the Cadmium Zinc Telluride films revealed polycrystalline nature with predominant (111) orientation of the cubic phase. With increase in Zn content in the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films, the other diffraction

peaks observed were corresponding to the (220), (311), (400), (331), (422) and (333) orientations.

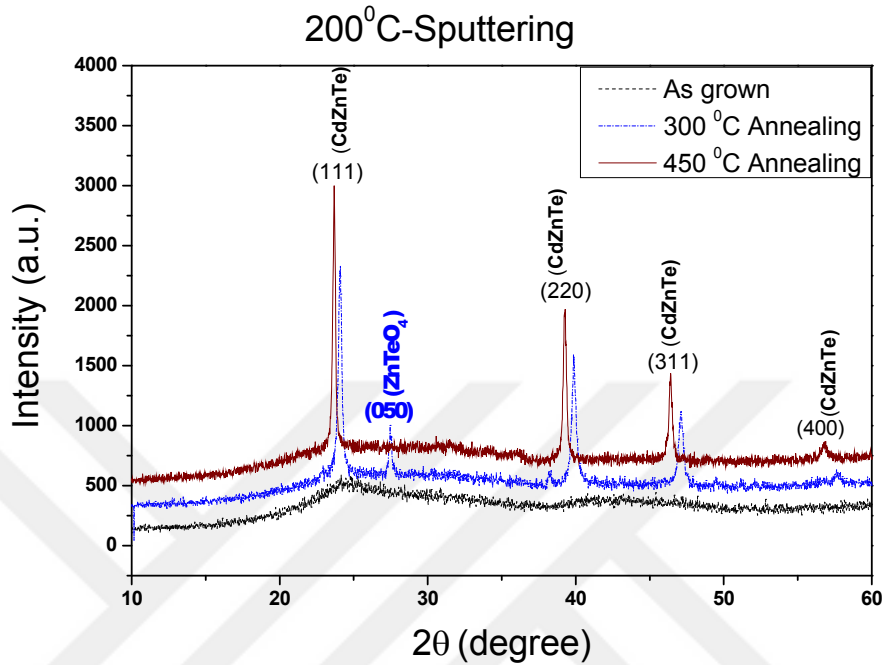


Figure 4.1: XRD measurements of CZT thin film samples Grown at 200°C, as performed with 300 and 450°C annealing under N₂ gases, respectively.

XRD measurement of a sample fabricated by RF sputtering technique at 200°C was performed, without annealing or doing any process. The other samples were annealed under N₂ and N₂H₂ gases at 300 and 450°C temperature and XRD spectra is shown in Figure 4.1. The crystallization behavior of the XRD measurements similar to that of the film Grown at 200°C under N₂ gases however second and third small picks was observed for this sample as well.

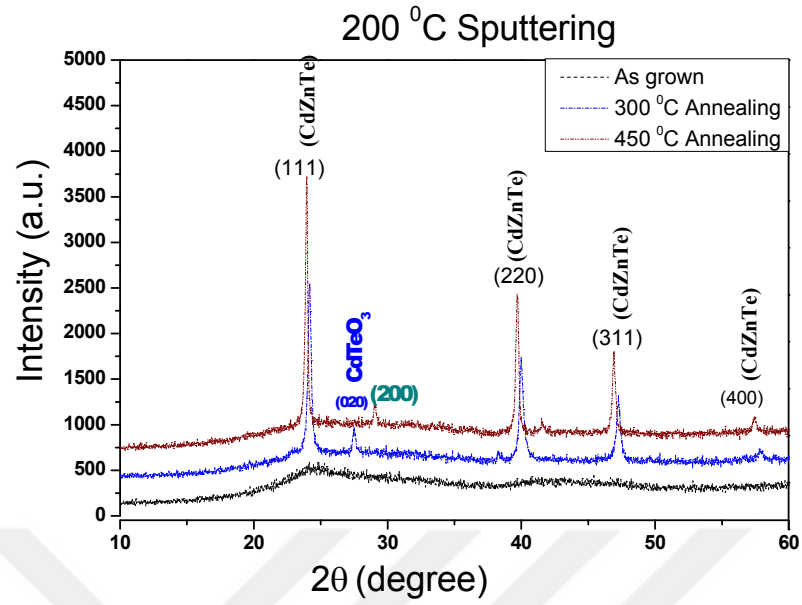


Figure 4.2: XRD measurements of CZT thin film samples Grown at 200°C, as performed with 300 and 450°C annealing under N_2H_2 gases, respectively.

Secondly, the film Grown at 300°C was annealed at 300 and 450°C under N_2 gases, and XRD measurements were performed (Figure 4.2). The crystallization behavior of the XRD measurements similar to that of the film Grown at 200°C was observed on this sample as well.

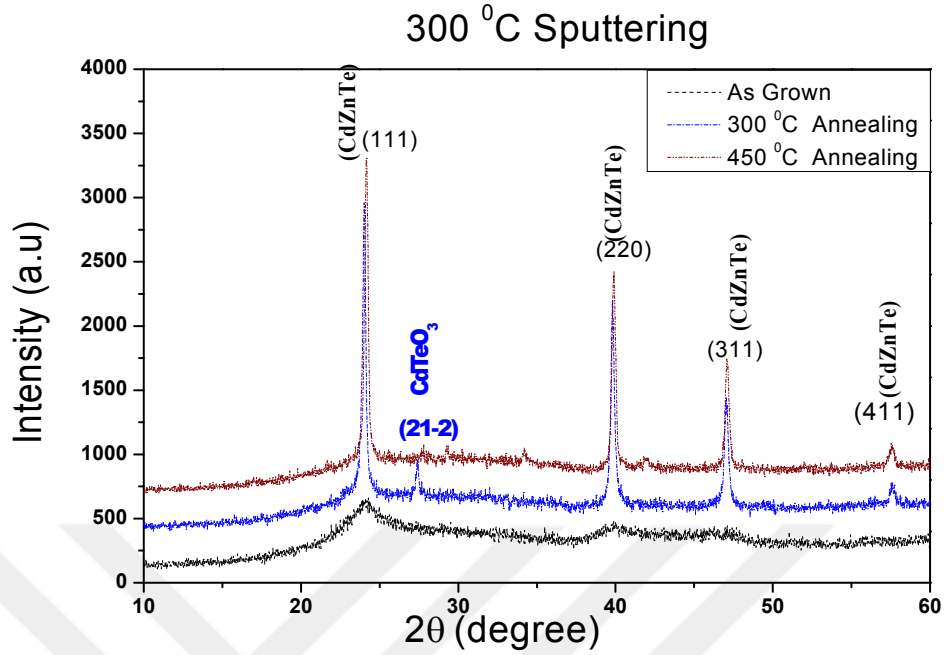


Figure 4.3: XRD measurements of CZT thin film samples Grown at 300°C, as performed with 300 and 450°C annealing under N₂ gases, respectively.

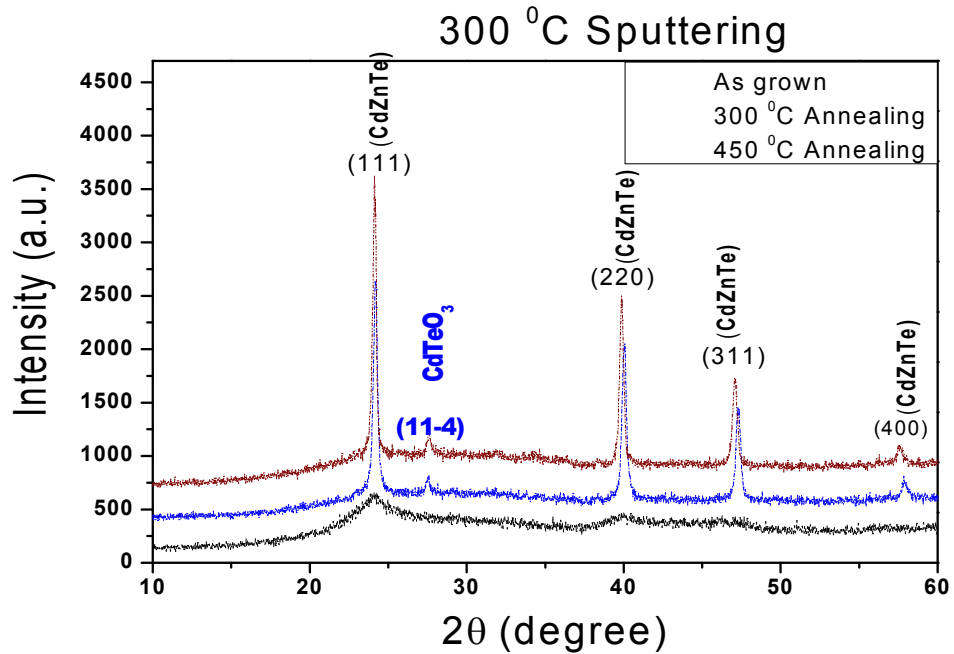


Figure 4.4. XRD measurements of CZT thin film samples Grown at 300°C as performed with 300 and 450°C annealing under N₂H₂ gases, respectively.

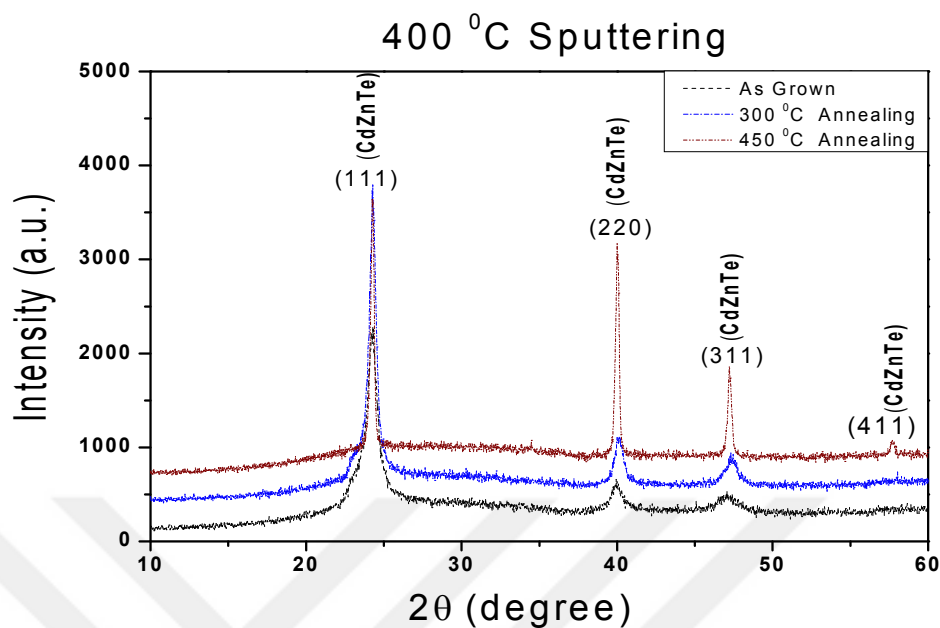


Figure 4.5 : XRD measurements of CZT thin film samples Grown at 400°C, as performed with 300 and 450°C annealing under N₂ gases, respectively.

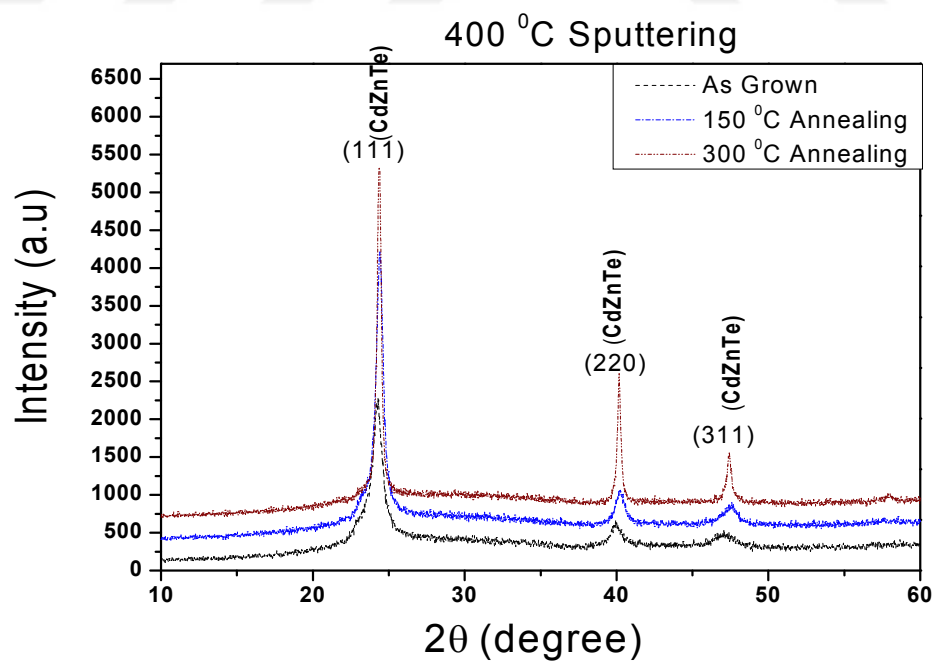


Figure 4.6 : XRD measurements of CZT thin film samples Grown at 400°C, as performed with 300 and 450°C annealing under N₂H₂ gases, respectively.

This result shows the improvement in composition of the film crystallinity in the CdZnTe lattice. The diffraction peaks at $2\theta = 24.3^\circ$, 40° and 47° , from figures 4.1-4.6 characteristic for cubic CdZnTe alloy, confirm the above assumption. Bragg's law is derived as $n\lambda=2d\sin(\theta)$, where n , λ , d , and θ are the order of diffracted beam, wavelength of the incident X-ray, inter-planar spacing of parallel planes, and Bragg's angle, respectively.

$$n\lambda=2d\sin(\theta) \quad (8)$$

where
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (9)$$

When d is put in the Braggs law :

$$\left(\frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}}\right)^2 = (n\lambda)^2 \quad (10)$$

Then, if $\sin\theta$ left alone on the left side:

$$4a \sin^2 \theta = \lambda^2 * (h^2 + k^2 + l^2) \quad (11)$$

Finally:
$$\sin^2 \theta = \frac{\lambda^2}{4a^2} * (h^2 + k^2 + l^2) \quad (12)$$

From this formula it can found a is equal to the a_x which used in Vegard's law to find x that the value of Zn in the compound. The average value of “ x ” observed d -values three XRD peaks using the following formula(Vegard's law):

$$a_{(Cd_{1-x}Zn_xTe)} = (1 - x) * a_{(CdTe)} + x * a_{(ZnTe)} \quad (13)$$

From the Vegard's law
$$x = \frac{a_{CdTe} - a_x}{a_{CdTe} - a_{ZnTe}} \quad (14)$$

where $a_{CdTe}=6.4810 \text{ \AA}$ and $a_{ZnTe}=6.1026 \text{ \AA}$. As an example x can be found from the 200°C sputtering temperature, and 300°C annealing. For the first peak $2\theta = 24.06^\circ$, $\theta=12.03^\circ$ and λ is a constant which is equal $2.37 \text{ \AA}$ and $a=6.4923 \text{ \AA}$ and miller indices (111) for the first peak which can be found from the ICDD XRD data base analysis program. All of the other miller indices and their compounds were found from ICDD XRD data base program that given in Table 2.

$$(\sin 12,03)^\circ = \frac{(2,37)^\circ}{4a^2} (1^2 + 1^2 + 1^2) \quad (15)$$

From Vegard's law
$$x = \frac{6.4810A^0 - 6.4923A^0}{6.4810A^0 - 6.1026A^0} = 0.222724 \quad (16)$$

Table 2: XRD measurements CdZnTe Thin films and analysis the peaks with ICDD database then calculated the x value and Eg, by using different deposition and annealing temperature under N₂ gases.

RF temperature °C	Annealing temperature °C	PEAK	2theta	a=dx	x values	Eg Calculated from (1.510+0.606X+0.139X ²)[80]	Eg calculated from (1.5045+0.631*X+0.128*X ²)[81]
200	As Grown	1 st	24.38	6.36	0.32	1.72	1.72
		2 nd	40.38	6.31	0.46	1.82	1.82
		3 rd	47.788	0	0	1.51	1.51
	300	1 st	24.06	6.37	0.30	1.7	1.7
		2 nd	39.84	6.37	0.29	1.7	1.7
		3 rd	47.08	6.37	0.28	1.69	1.69
	450	1 st	23.746	6.43	0.13	1.59	1.59
		2 nd	39.24	6.41	0.18	1.62	1.62
		3 rd	46.38	6.42	0.17	1.62	1.62
300	As Grown	1 st	24.16	6.37	0.30	1.7	1.7
		2 nd	39.68	6.35	0.35	1.74	1.74
		3 rd	0	0	0	1.51	1.5
	300	1 st	24	6.37	0.31	1.71	1.71
		2 nd	39.78	6.37	0.31	1.71	1.71
		3 rd	47.02	6.37	0.30	1.7	1.7
	450	1 st	24.14	6.38	0.27	1.68	1.68
		2 nd	39.86	6.39	0.24	1.66	1.66
		3 rd	47.06	6.39	0.23	1.66	1.66
450	As Grown	1 st	24.24	6.35	0.35	1.74	1.74
		2 nd	39.94	6.37	0.28	1.69	1.69
		3 rd	47.02	6.4	0.22	1.65	1.65
	300	1 st	24.3	6.31	0.46	1.81	1.82
		2 nd	40.1	6.34	0.39	1.76	1.77
		3 rd	47.36	6.33	0.40	1.78	1.78
	450	1 st	24.26	6.32	0.43	1.79	1.8
		2 nd	40	6.34	0.36	1.75	1.75
		3 rd	47.22	6.35	0.34	1.73	1.73

As the annealing temperature increases the peak intensity also increases as seen in figures 4.1-4.6. This result shows that annealing process is to supply the movement freedom of the Cd, Zn and Te atoms to form the crystalline structure. One can conclude that, the heat treatment of such samples determines the total inclusions of the Zn atoms in the CdTe lattice and the precipitation in crystalline form of the residual free Te atoms. From these figures it can be seen that with the increase of RF sputtering temperature, the crystallinity also increases.

4.1.2 Energy Dispersive X-ray (EDX) Analysis Measurements

The chemical composition of source and deposited CdZnTe thin films were investigated by using energy dispersive X-ray analysis (EDX or EDS) measurements. The results are shown in Figures 4.7-4.14 respectively. A typical EDS spectrum obtained from the samples Grown at 0-300-400°C sputtering temperature and annealed at 0-300-450°C temperature. In this study, another method which is used to investigate bandgap of CdZnTe thin films is the EDXA. We calculated x values from the figures as follows firstly the atomic weight of Cd and Zn in the CZT composition is found and then x value computed from calculation 16.

At the same time we found the percent value of Cd, Zn, and Te then listed in the table 4-2. The results show that powder has a nearly a stoichiometric composition. With the change of the temperature, the atomic ratio of Cd: Zn; Te also changed. The ratio of this changeable is given, in the Table 3. The EDXA measurement was operated at acceleration energy to measure the composition at depth since the range of electron penetration depends on the incident electron-beam energy. An electron beam with relatively 20 kV was chosen for the deep layers. When annealing temperature varies from 0 to 450°C, and the deposition temperature varies from 200 to 400°C it was observed that there is an atomic percentage of irregular Zn increase at 200°C deposition temperatures with increase of annealing temperature. However at 300°C RF sputtering temperature when the annealing temperature is increased the atomic percentage of Zn decreases. Also atomic percentage of Zn increased with the increase of annealing temperature to 400°C RF sputtering temperature. The atomic

percentages of Cd and Te change with the change of the temperature RF sputtering and annealing as seen in the table 4.3.

Table 3: Atomic percentage (% value) of Cd; Zn; Te; in the compound found from EDXA.

RF sputtering temperature °C	Annealing temperature °C	% value of Cd from EDXA	% value of Zn from EDXA	% value of Te from EDXA	Summation of %Cd;Zn;Te in the compaund
200	0	9.86	3.33	17.26	30.45
200	300	16.62	8.14	39.46	64.22
200	450	21.25	8.97	24.13	54.35
300	0	28.35	16.34	47.46	92.15
300	300	22.34	10.21	34.08	66.63
300	450	19.16	9.61	34.08	62.85
400	0	22.95	7.79	36.82	60.56
400	300	22.85	8.96	38.09	69.90
400	450	20.81	9.32	33.23	63.36

Then for calculating the x value we researched the atomic weight percentage of Zn and Cd in the compound from the figures. All of these results are given in the table 4.4. x can be calculated with the help of the following formula from each figure.

$$x = \frac{Zn}{Zn + Cd} \quad (16)$$

From figure 4.7. 200°C sputtering temperature and 0°C annealing temperature

$$x = \frac{AtomicWeightofZn}{AtomicWeightofZn + AtomicWeightofCd} = \frac{10.89}{10.89 + 7.47} = 0.593 \quad (17)$$

From figure 4.7. 200°C sputtering temperature and 0°C annealing temperature

$$x = \frac{12.97}{12.97 + 15.95} = 0.448 \quad (18)$$

From the other figures x can be calculated in the same way then all of the x values can be found in the table 4.4.

It can be seen from the figures 4.7-4.17 the summation of atomic percentage of Cd, Zn, Te was not 100%. Their rates are average 50-60% the others are Si (silicon), Mg, (magnesium), C (carbon), O (oxygen), and Na (sodium).

Table 4: X value calculation which is made according to EDX measurements from the atomic weight of Cd and Zn.

RF sputtering temperature °C	Annealing temperature °C	Atomic Weight of Zn(%)	Atomic Weight of Cd(%)	X value from EDXA ($x = \frac{Zn}{Zn + Cd}$)
200	0	1.50	2.58	0.433
200	300	5.72	6.79	0.445
200	450	5.19	7.15	0.495
300	0	17.21	17.37	0.498
300	300	7.64	9.72	0.432
300	450	6.67	7.71	0.478
400	0	6.01	10.28	0.423
400	300	6.54	9.71	0.398
400	450	6.56	5.52	0.492

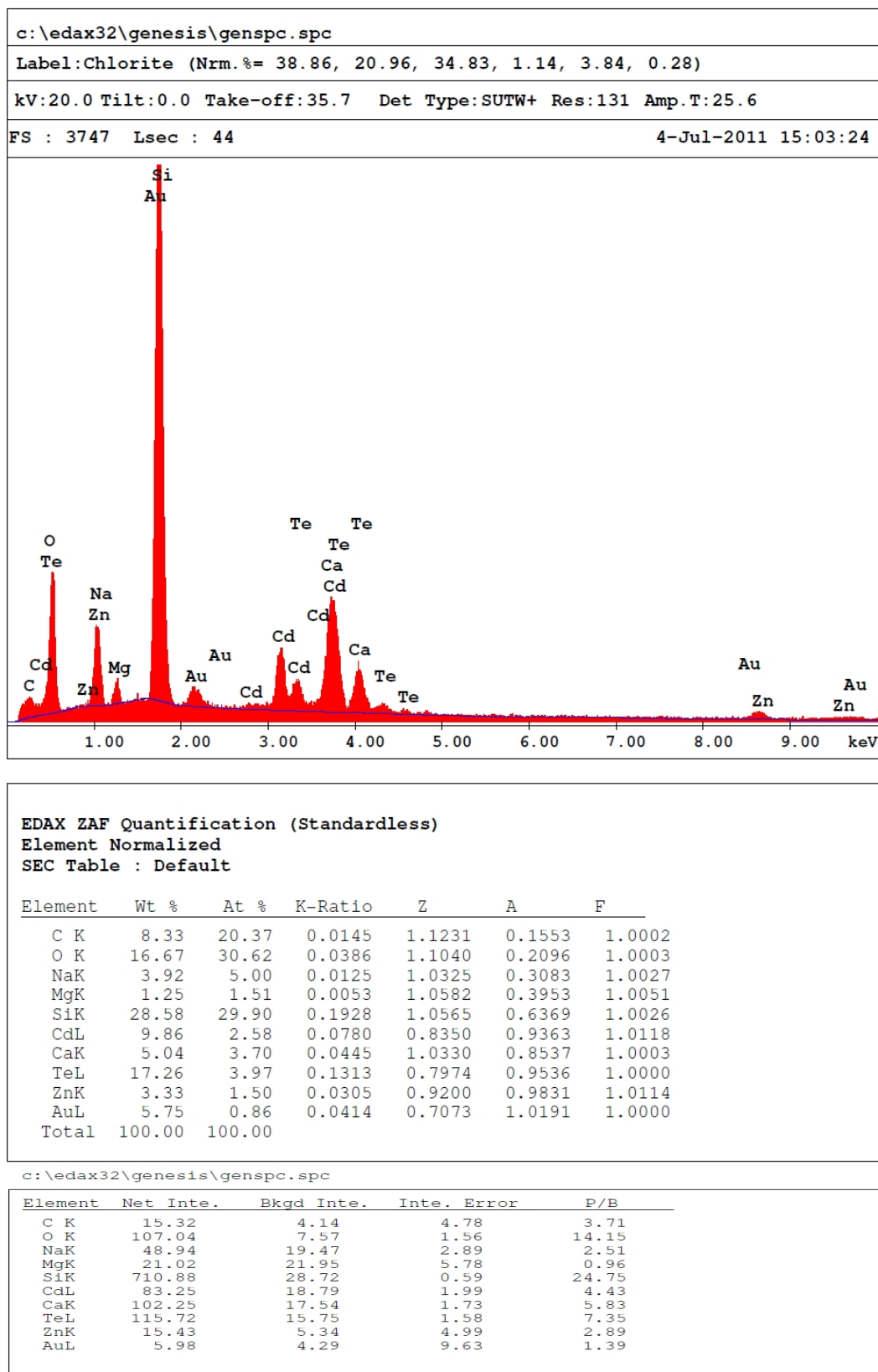
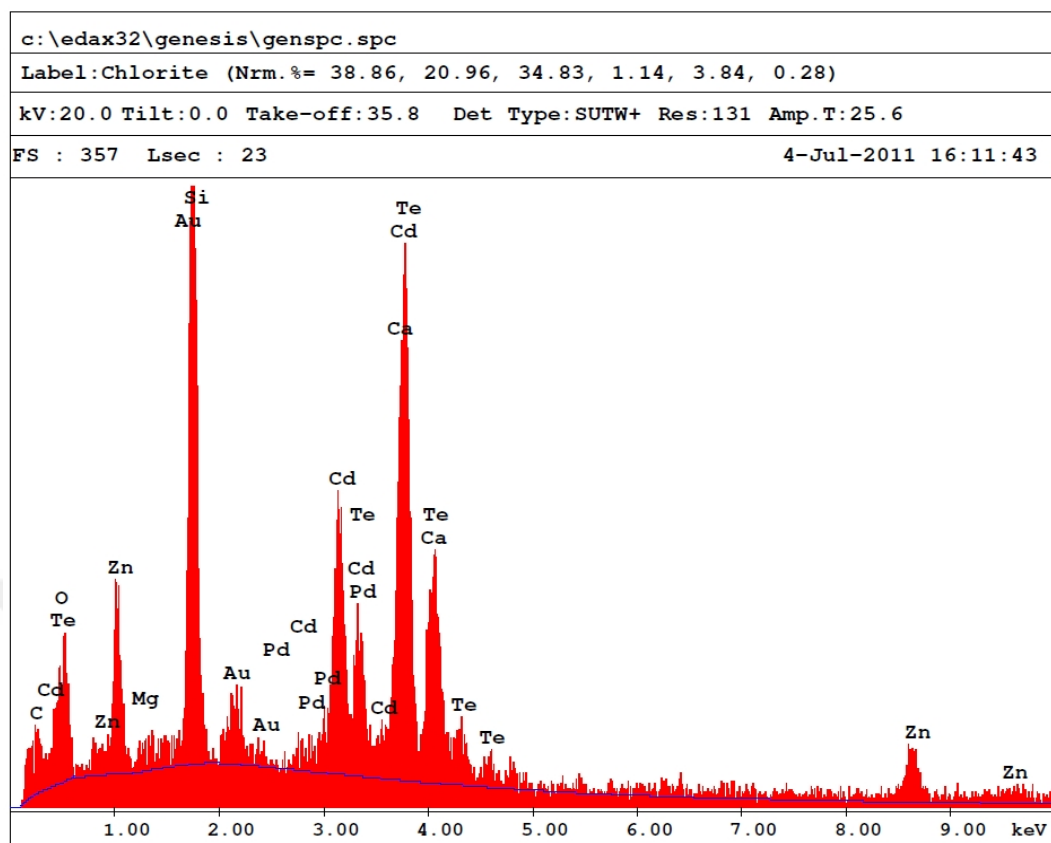


Figure 4.7: EDX spectra of CdZnTe thin films samples Grown at 200°C sputtering temperature and under 0°C annealing temperature.



EDAX ZAF Quantification (Standardless)
 Element Normalized
 SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	7.62	29.15	0.0195	1.2218	0.2089	1.0001
O K	5.63	16.18	0.0143	1.2005	0.2108	1.0002
MgK	0.94	1.78	0.0032	1.1496	0.2951	1.0026
SiK	13.30	21.76	0.0786	1.1469	0.5133	1.0040
AuM	4.72	1.10	0.0332	0.8293	0.8466	1.0003
PdL	1.09	0.47	0.0091	0.9248	0.8841	1.0156
CdL	16.62	6.79	0.1451	0.9138	0.9369	1.0198
CaK	2.47	2.83	0.0232	1.1290	0.8304	1.0006
TeL	39.46	14.21	0.3162	0.8713	0.9197	1.0000
ZnK	8.14	5.72	0.0805	1.0190	0.9644	1.0062
Total	100.00	100.00				

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Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	6.64	1.29	8.23	5.13
O K	18.10	2.46	4.76	7.37
MgK	2.65	6.50	26.83	0.41
SiK	110.64	10.18	1.86	10.87
AuM	0.65	10.34	128.45	0.06
PdL	1.74	9.08	46.04	0.19
CdL	70.06	9.44	2.42	7.42
CaK	26.11	9.02	4.57	2.90
TeL	90.36	8.18	2.06	11.05
ZnK	16.19	1.55	4.88	10.44

Figure 4.8: EDX spectra of CdZnTe thin films samples Grown at 200°C sputtering temperature and under 300°C annealing temperature.

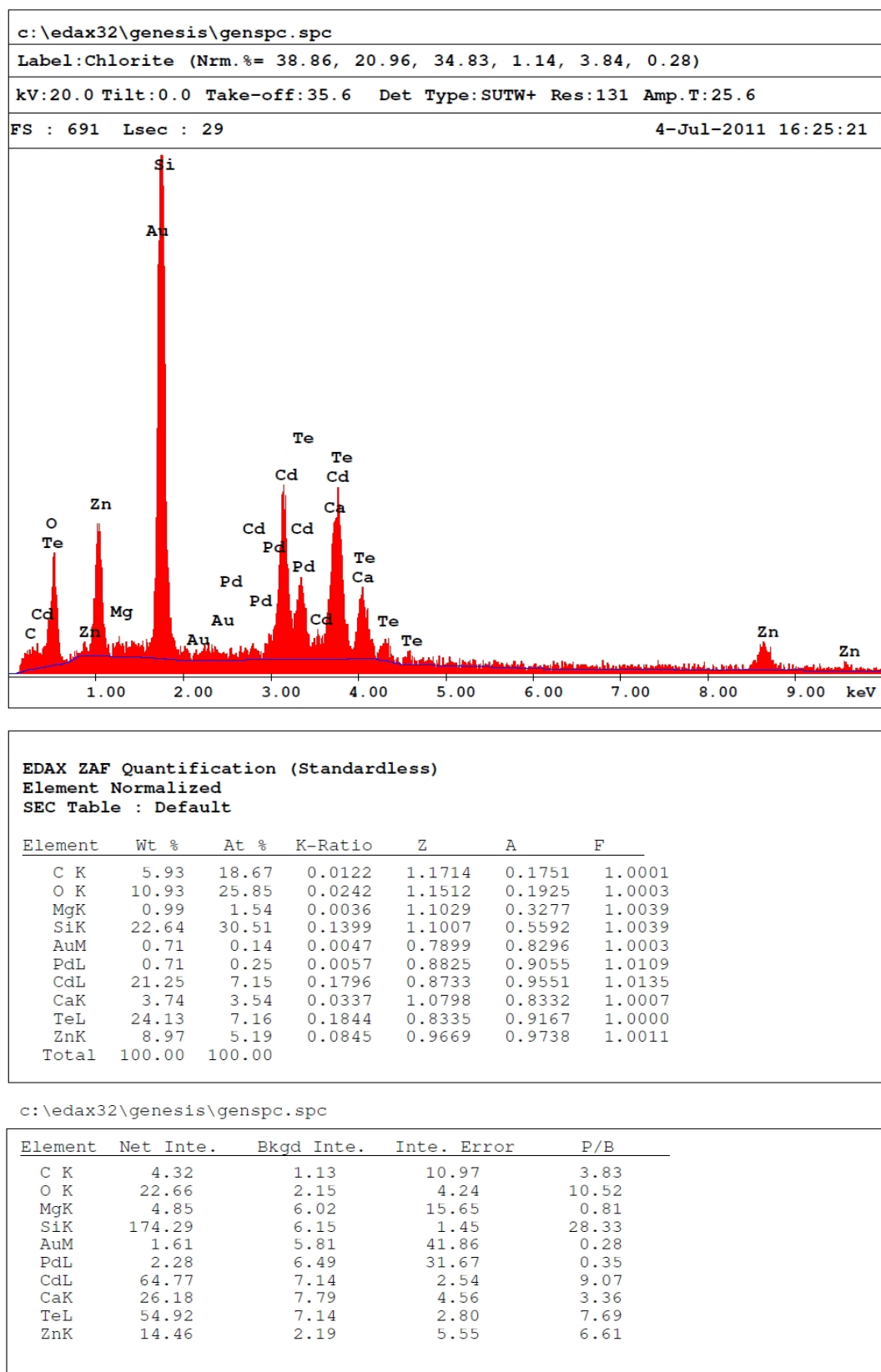
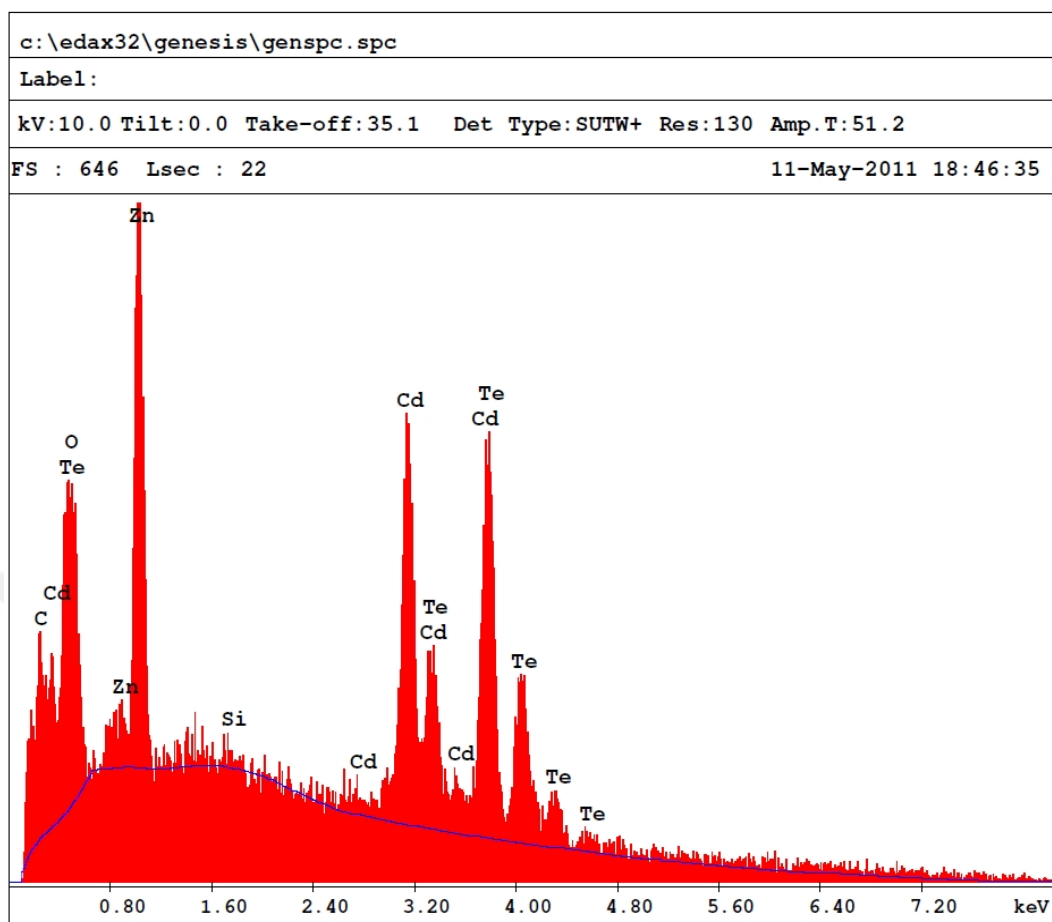


Figure 4.9: EDX spectra of CdZnTe thin films samples Grown at 200°C sputtering temperature and under 450°C annealing temperature.



EDAX ZAF Quantification (Standardless)

Element Normalized

SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	4.46	25.59	0.0264	1.3927	0.4246	1.0000
O K	3.19	13.71	0.0177	1.3578	0.4097	1.0002
ZnL	16.34	17.21	0.0933	1.0889	0.5245	1.0003
SiK	0.21	0.51	0.0020	1.2966	0.7339	1.0026
CdL	28.35	17.37	0.2723	0.9576	0.9887	1.0147
TeL	47.46	25.61	0.4147	0.9017	0.9691	1.0000
Total	100.00	100.00				

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Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	40.52	11.68	4.15	3.47
O K	51.25	20.58	3.95	2.49
ZnL	163.71	38.59	1.99	4.24
SiK	4.51	43.37	44.52	0.10
CdL	145.25	26.60	2.04	5.46
TeL	149.99	20.14	1.93	7.45

Figure 4.10: EDX spectra of CdZnTe thin films samples Grown at 300°C sputtering temperature and under 0°C annealing temperature.

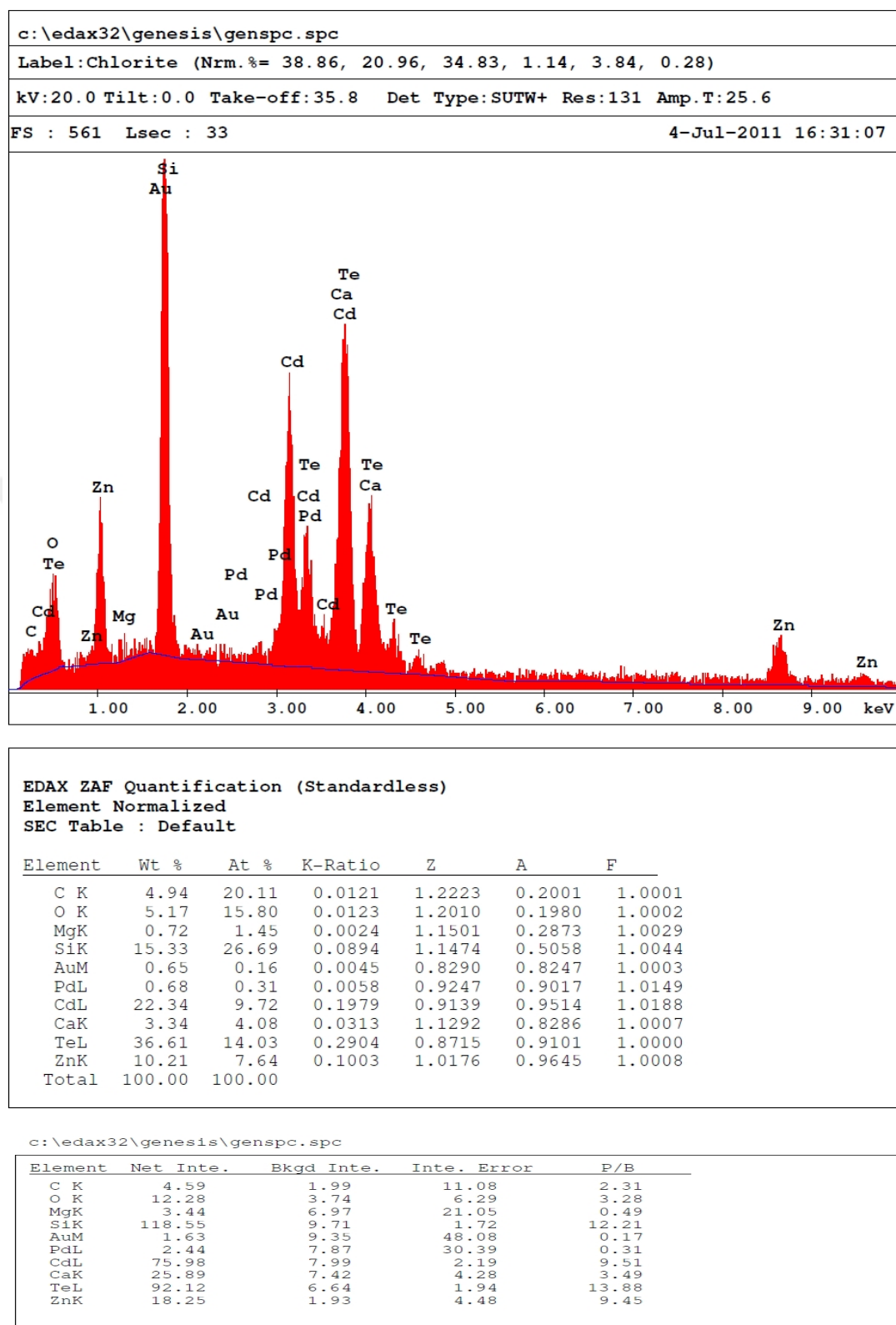


Figure 4.11: EDX spectra of CdZnTe thin films samples Grown at 300°C sputtering temperature and under 300°C annealing temperature.

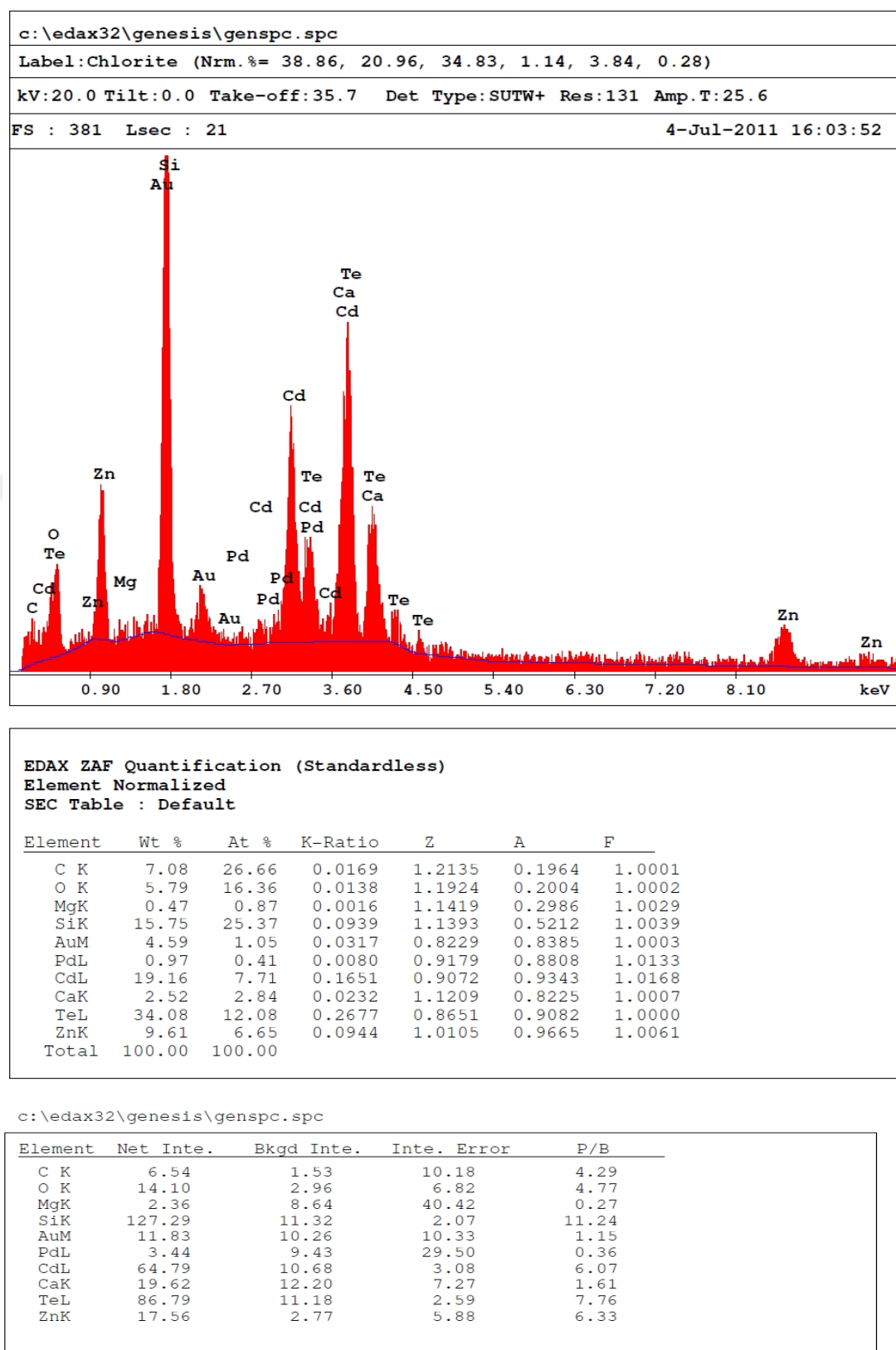
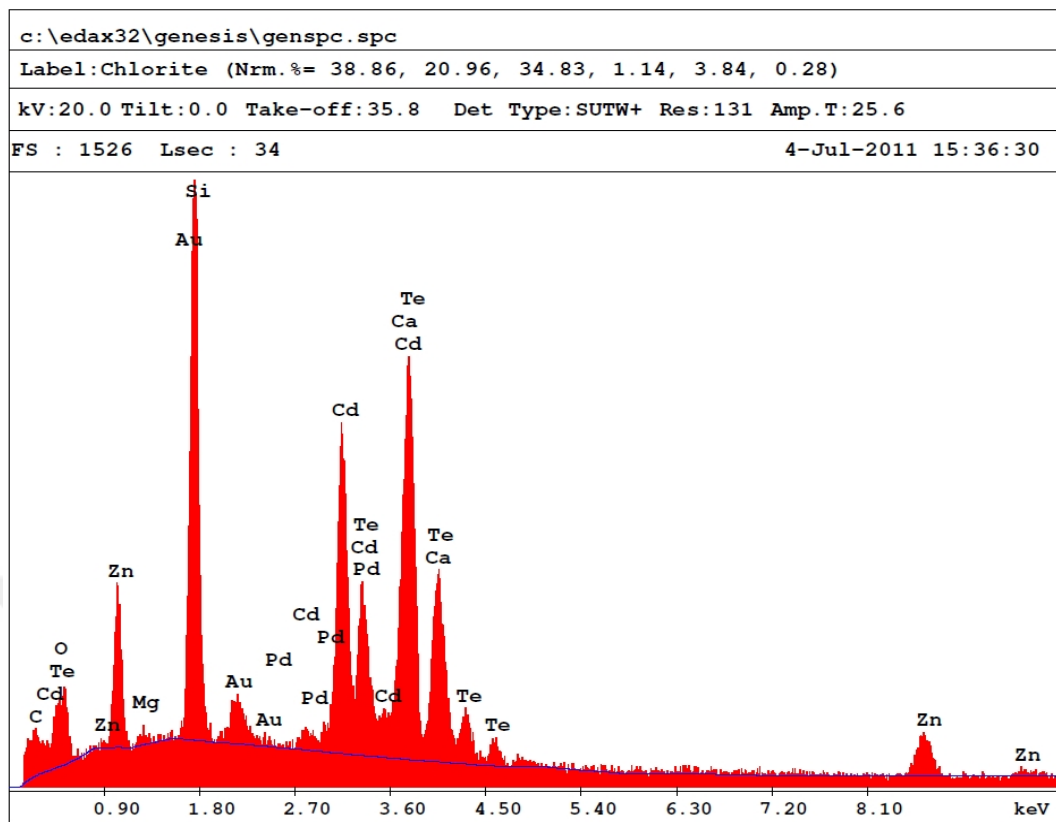


Figure 4.12: EDX spectra of CdZnTe thin films samples Grown at 300°C sputtering temperature and under 450°C annealing temperature.



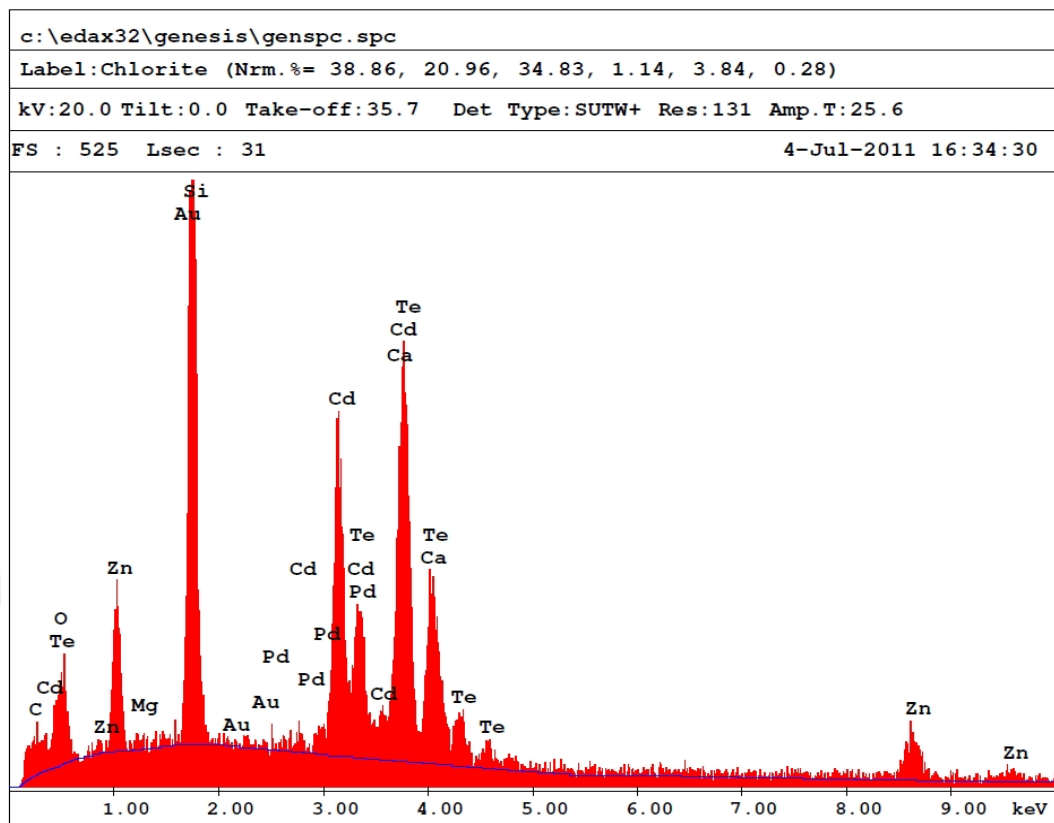
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	6.19	25.96	0.0159	1.2322	0.2083	1.0001
O K	3.77	11.87	0.0088	1.2107	0.1920	1.0002
MgK	0.39	0.81	0.0013	1.1592	0.2931	1.0028
SiK	14.17	25.42	0.0845	1.1564	0.5131	1.0044
AuM	4.08	1.04	0.0287	0.8373	0.8398	1.0003
PdL	0.94	0.45	0.0079	0.9334	0.8847	1.0140
CdL	22.95	10.28	0.2018	0.9221	0.9373	1.0177
CaK	2.90	3.64	0.0269	1.1390	0.8147	1.0005
TeL	36.82	14.53	0.2896	0.8790	0.8949	1.0000
ZnK	7.79	6.01	0.0776	1.0291	0.9626	1.0052
Total	100.00	100.00				

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Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	16.12	5.23	5.45	3.08
O K	23.36	9.67	4.77	2.41
MgK	5.08	24.52	24.66	0.21
SiK	298.95	30.68	1.08	9.75
AuM	28.03	31.52	5.80	0.89
PdL	8.91	26.58	15.07	0.34
CdL	206.83	26.81	1.33	7.71
CaK	59.29	24.52	2.99	2.42
TeL	245.12	21.96	1.18	11.16
ZnK	37.68	13.48	3.64	2.80

Figure 4.13: EDX spectra of CdZnTe thin films samples Grown at 400°C sputtering temperature and under 0°C annealing temperature.



EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	6.00	23.85	0.0147	1.2212	0.2010	1.0001
O K	4.65	13.89	0.0111	1.1999	0.1993	1.0002
MgK	0.45	0.87	0.0015	1.1491	0.2902	1.0030
SiK	16.19	27.53	0.0952	1.1464	0.5103	1.0044
AuM	0.00	0.00	0.0000	0.8281	0.8239	1.0003
PdL	0.00	0.00	0.0000	0.9238	0.9059	1.0153
CdL	22.85	9.71	0.2031	0.9130	0.9548	1.0194
CaK	2.81	3.35	0.0264	1.1281	0.8326	1.0006
TeL	38.09	14.25	0.3030	0.8706	0.9136	1.0000
ZnK	8.96	6.54	0.0878	1.0165	0.9640	1.0000
Total	100.00	100.00				

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Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	5.34	2.02	10.18	2.65
O K	10.61	3.72	7.10	2.86
MgK	2.05	8.19	37.21	0.25
SiK	120.63	10.20	1.75	11.82
AuM	0.00	11.02	0.00	0.00
PdL	0.00	9.19	0.00	0.00
CdL	74.50	9.26	2.30	8.05
CaK	20.87	8.38	5.22	2.49
TeL	91.82	7.53	2.00	12.20
ZnK	15.27	2.87	5.33	5.33

Figure 4.14: EDX spectra of CdZnTe thin films samples Grown at 400°C sputtering temperature and under 300°C annealing temperature.

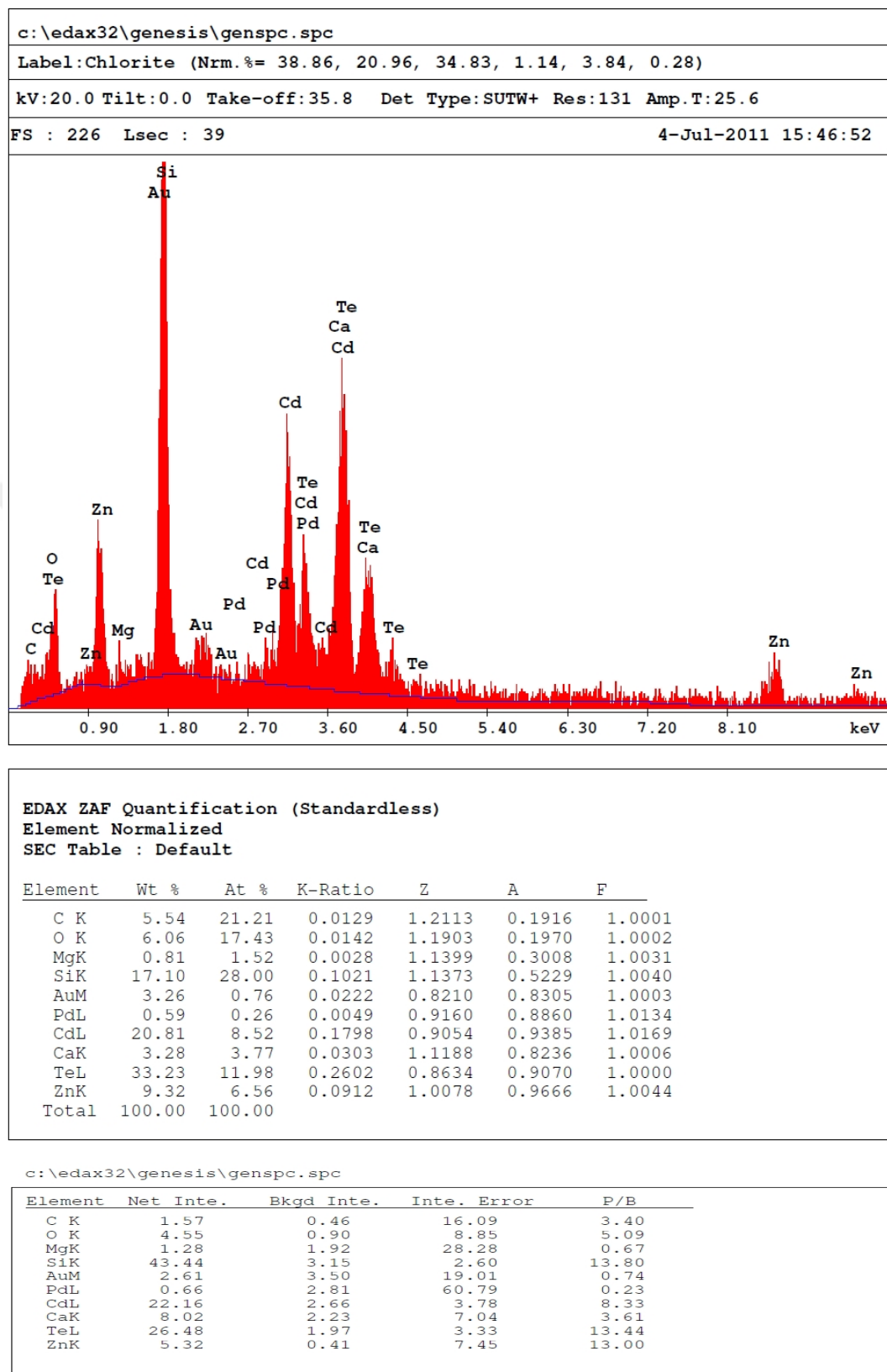


Figure 4.15: EDX spectra of CdZnTe thin films samples Grown at 400°C sputtering temperature and under 450°C annealing temperature.

4.1.3. Scanning Electron Microscopy (SEM)

An electron beam is used by an electron microscope for producing a magnified image of the sample. The image in Scanning Electron Microscopy SEM is produced by scanning the sample with a focused electron beam and detecting the secondary or backscattered electrons [82]. As it is shown in the Figures 4.15-4.21, uniformity of sample surface is increased after the post-annealing process. Throughout the surface, there are accumulations which are large randomly distributed before the annealing process and they are observed through images. Those accumulations cause incomplete solid reaction as the thermal energy that is derivated from driving force does not exist or insufficient. The accumulations nearly disappear and ended in a smoother, thicker and more uniformed shape thanks to the thermal energy caused by the post- annealing process. Figure 4.15 shows the SEM images of the samples deposited at 200°C and as Grown images (a) are 5µm and (b) is 1 µm, (b) shows the larger grain size. Figures 4.16 show the SEM images of the samples which deposited at substrate temperature of 200°C and 300°C annealed images 5µm, 1µm respectively. Also figure 4.16 a and b shows SEM images of the sample deposited at substrate temperature 200°C annealed at 300°C 5µm-1µm respectively, with increasing the temperature SEM image getting larger grain size whose means sample is getting crystallinity. Figure 4.17 shows SEM image of the samples deposited at substrate temperature of 200°C and annealed at 450°C images 5µm, 1µm respectively. It can be seen that from the figure 4.17 with the increase of the annealing temperature, Te evaporates after a definite point, so we can see the hill and the gaps in the SEM images. Figure 4.18 shows SEM image of the samples deposited at substrate temperature of 300°C and under as Grown, Images 5µm, 1µm and 500nm respectively. Concurrently this figure shows SEM images which image 5mm, 1mm, 0.5mm, figure c has larger grain size than other. And also c has an ordered structure than a and b. Figures 4.20-4.21 and 4.22 show SEM images deposited at 400°C and as Grown, annealed at 300, 450°C respectively. Especially in Fig 4.22-c, images confirm the improvement of crystallinity. It can be seen from the Figures 4.15-4.21 that SEM images show it getting uniformly and crystallinity when images are in smaller size, and with increasing deposition and annealing temperature.

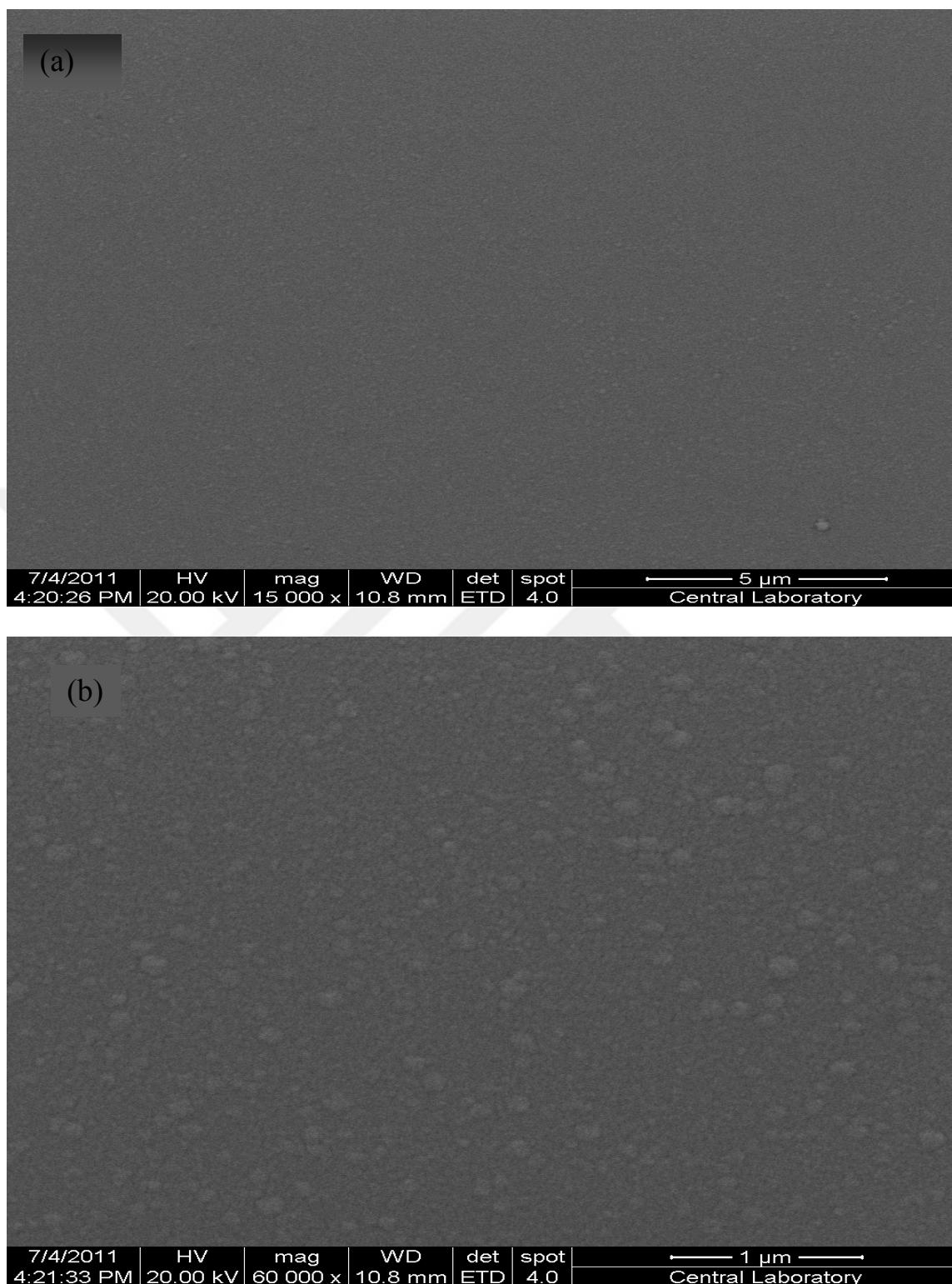


Figure 4.15: SEM image of the samples deposited at substrate temperature of 200°C and as Grown images (a)-5μm , (b)-1μm respectively.

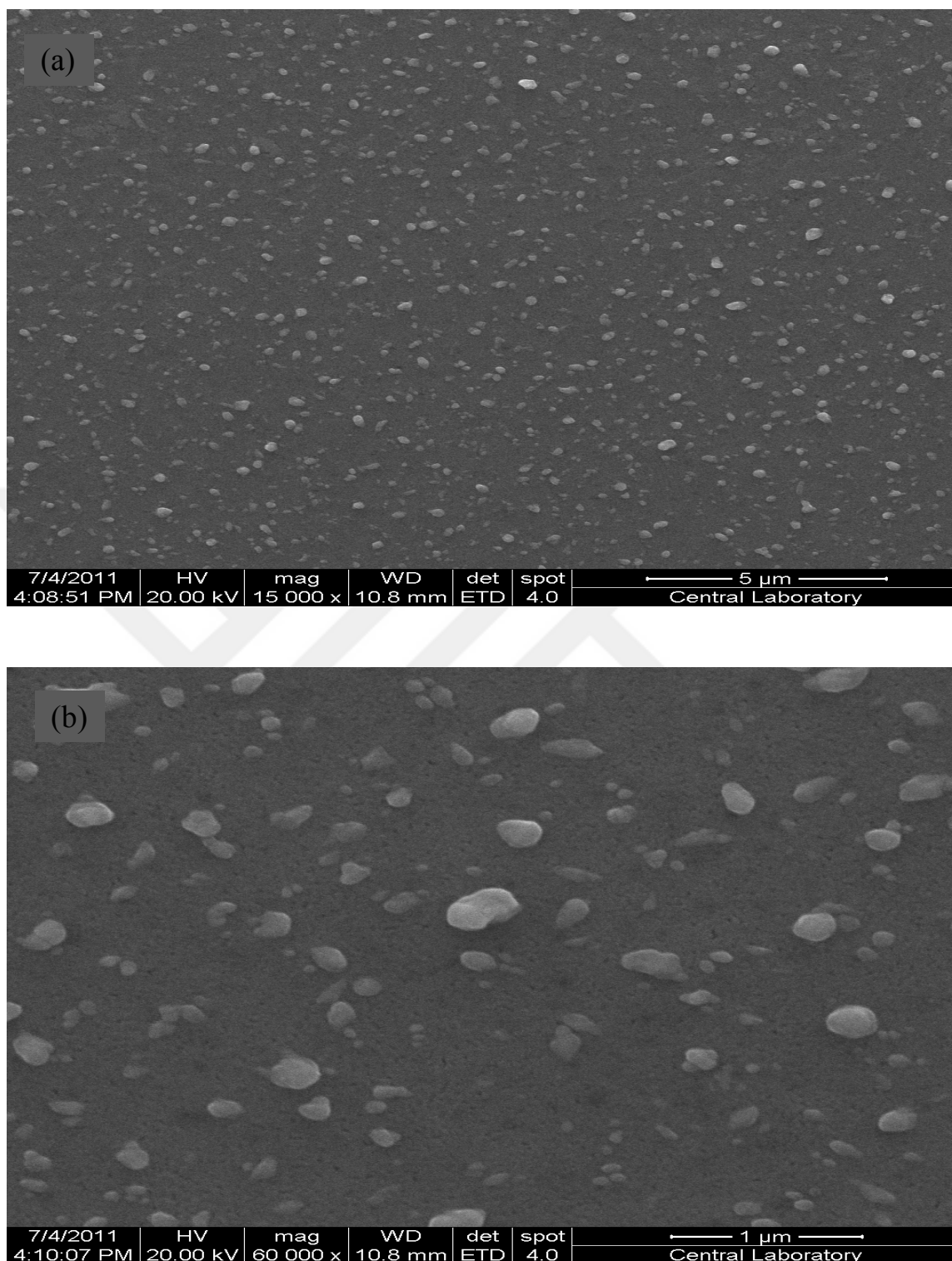


Figure 4.16: SEM image of the samples deposited at substrate temperature of 200°C and 300°C annealed images (a)-5 μ m, (b)-1 μ m respectively.

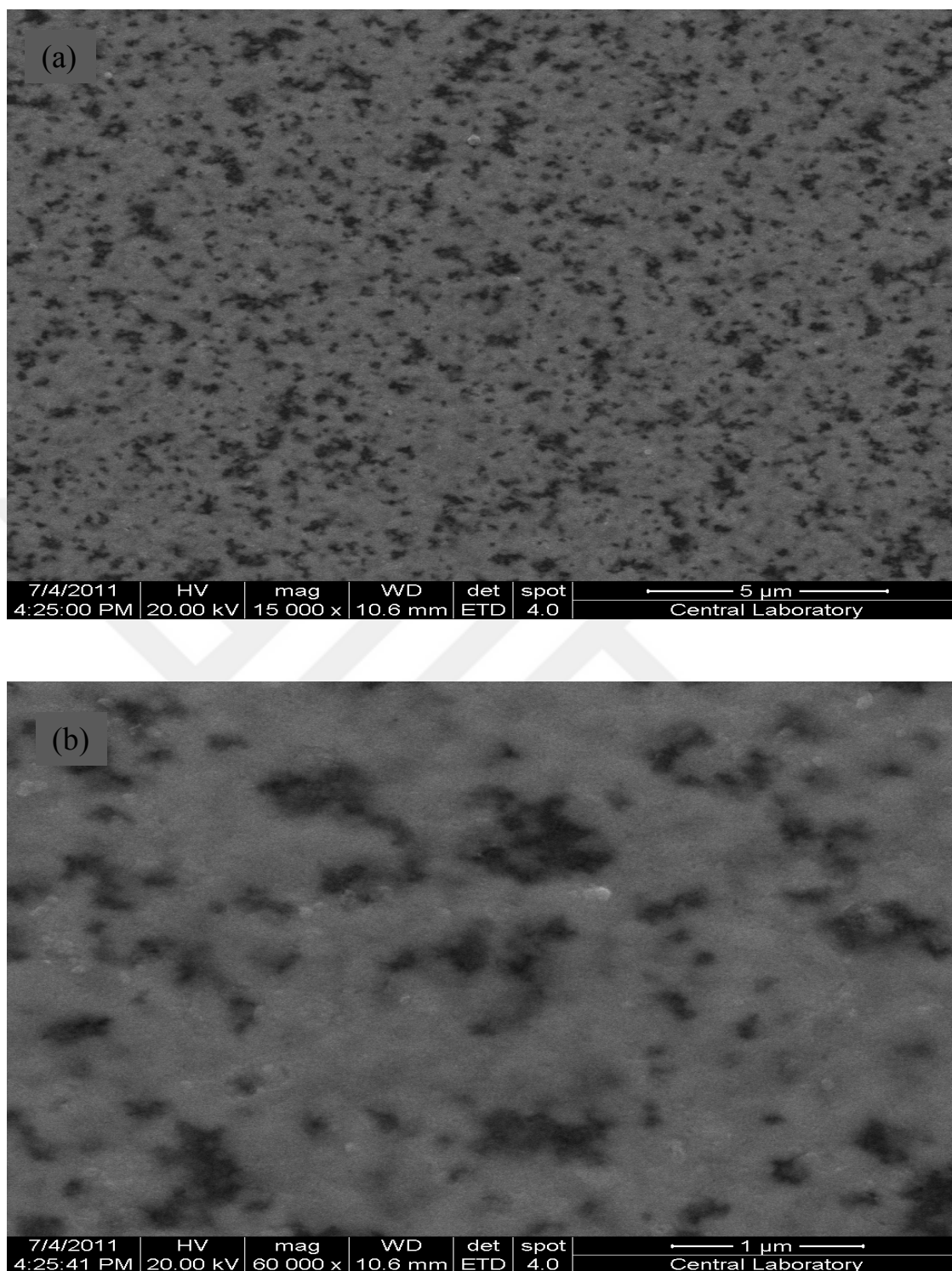


Figure 4.17: SEM image of the samples deposited at substrate temperature of 200°C and annealed at 450°C images (a)-5 μ m, (b)-1 μ m respectively.

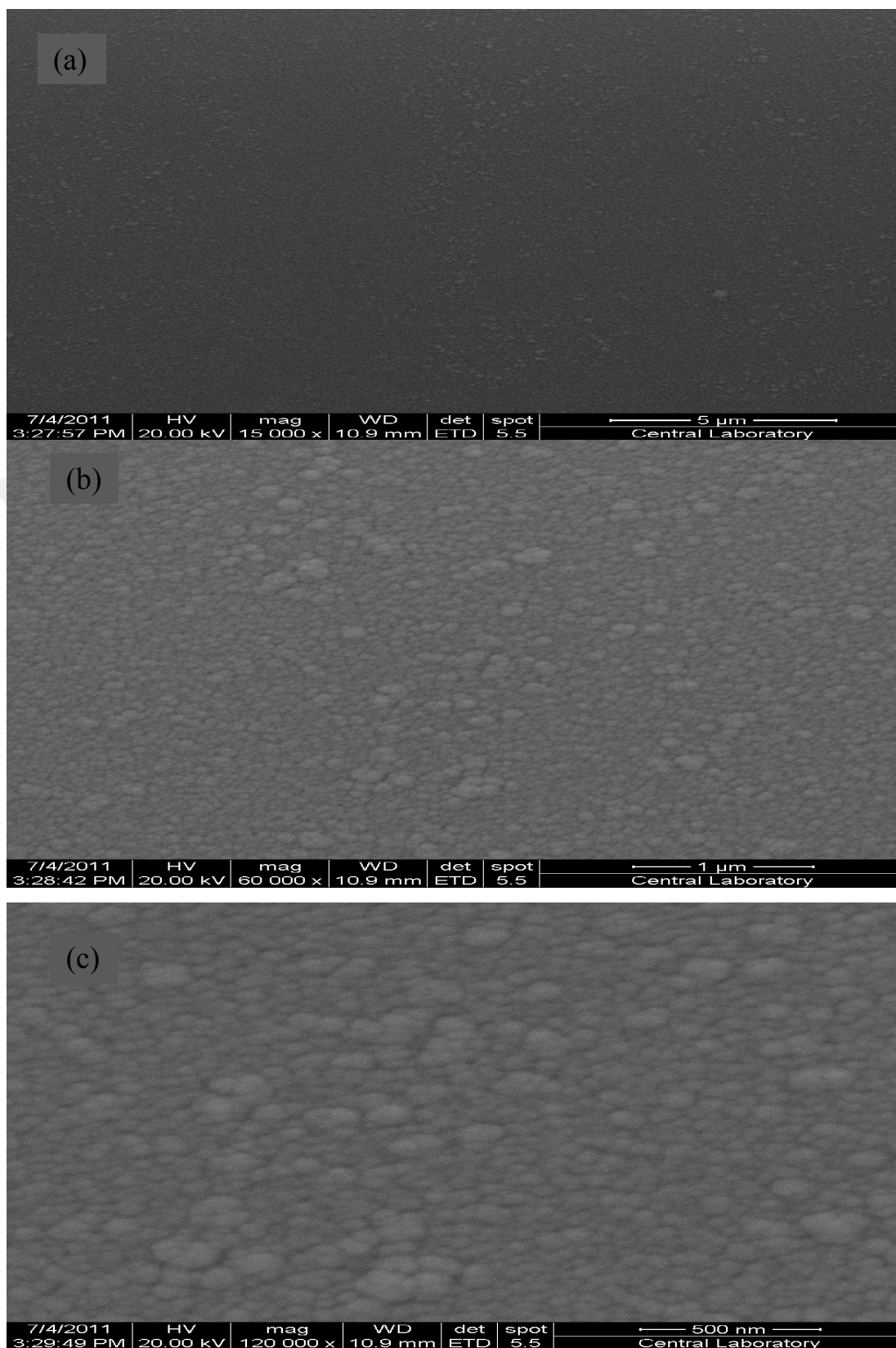


Figure 4.18: SEM image of the sample at substrate temperature of 300°C and as Grown images (a)-5 μm , (b)-1 μm , (c)- 500nm respectively.

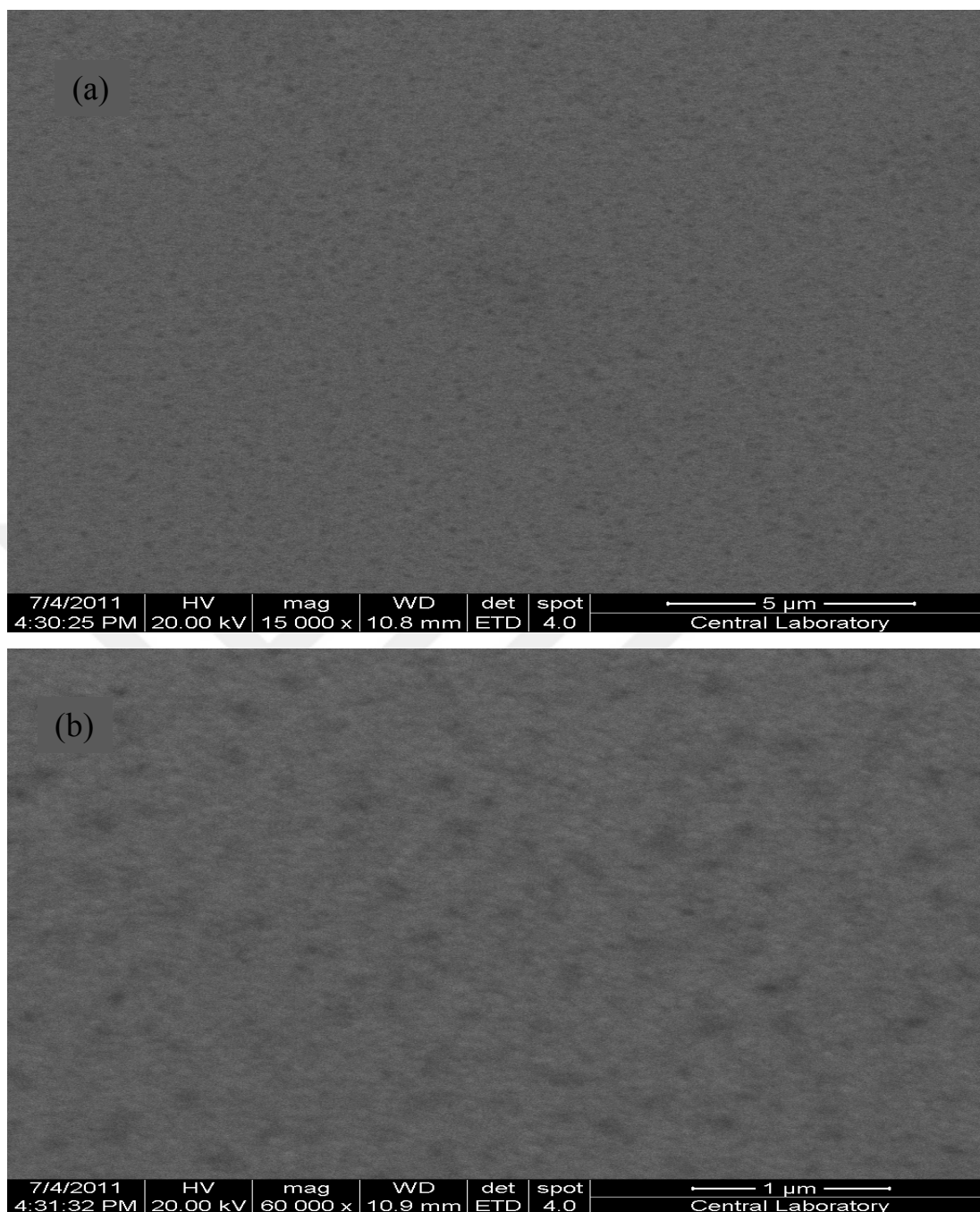


Figure 4.19: SEM image of the samples deposited at substrate temperature of 300°C and annealed 300°C, images 5μm, 1μm respectively.

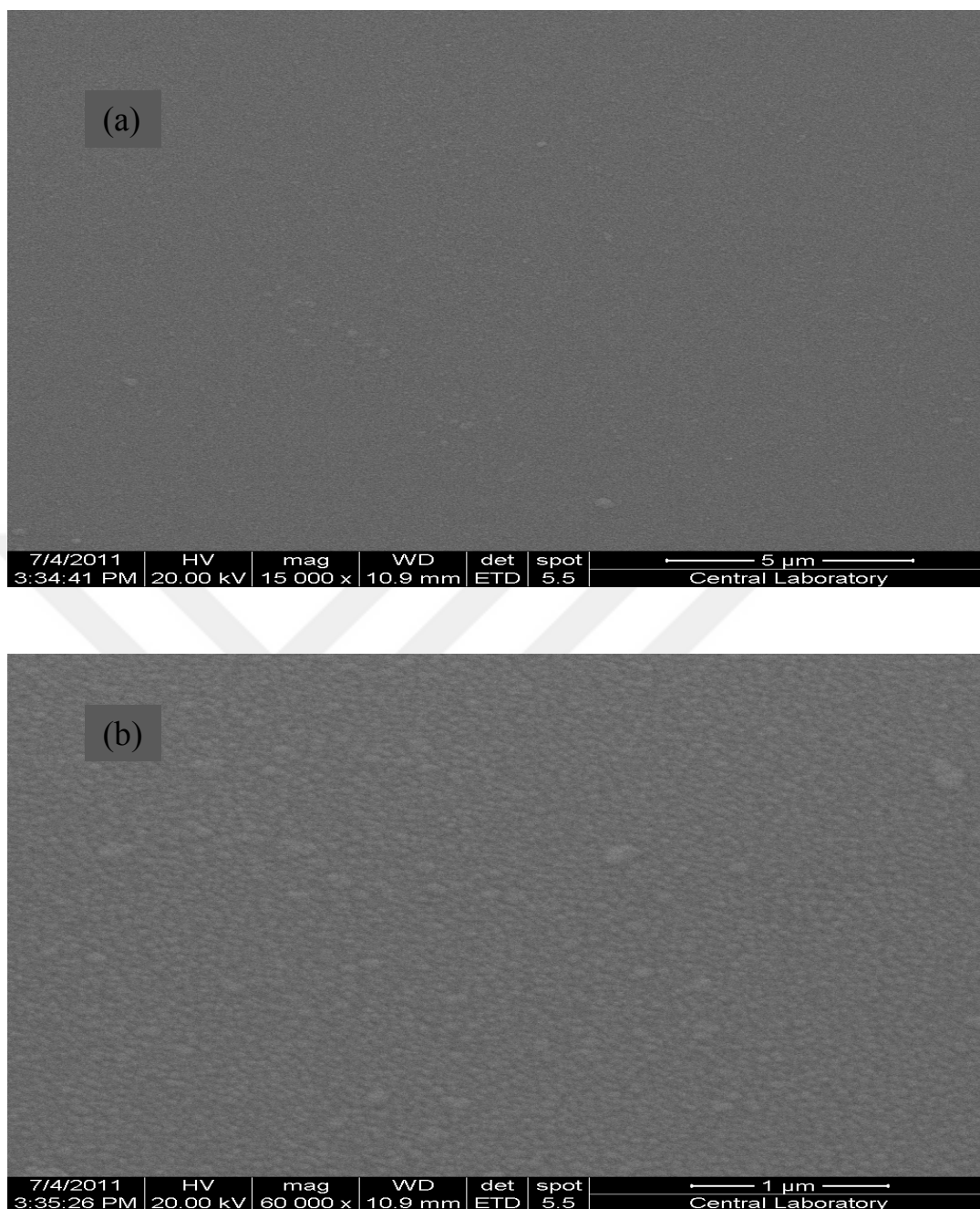


Figure 4.20: SEM image of the samples deposited at substrate temperature of 400°C and under as Grown, images 5μm, 1μm respectively.

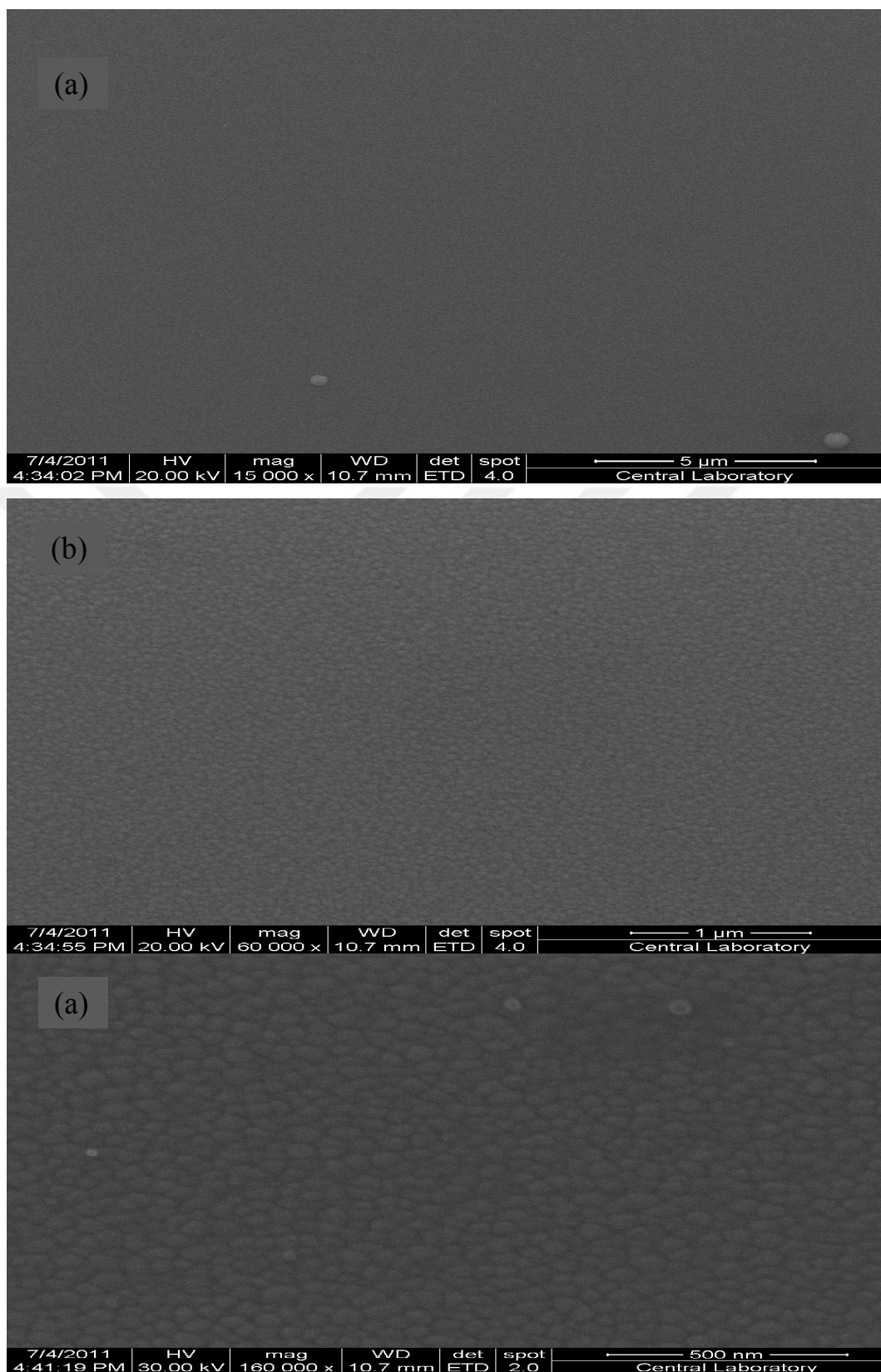


Figure 4.21: SEM image of the samples deposited at substrate temperature of 400°C and annealed 300°C, images 5 μ m, 1 μ m and 500nm respectively.

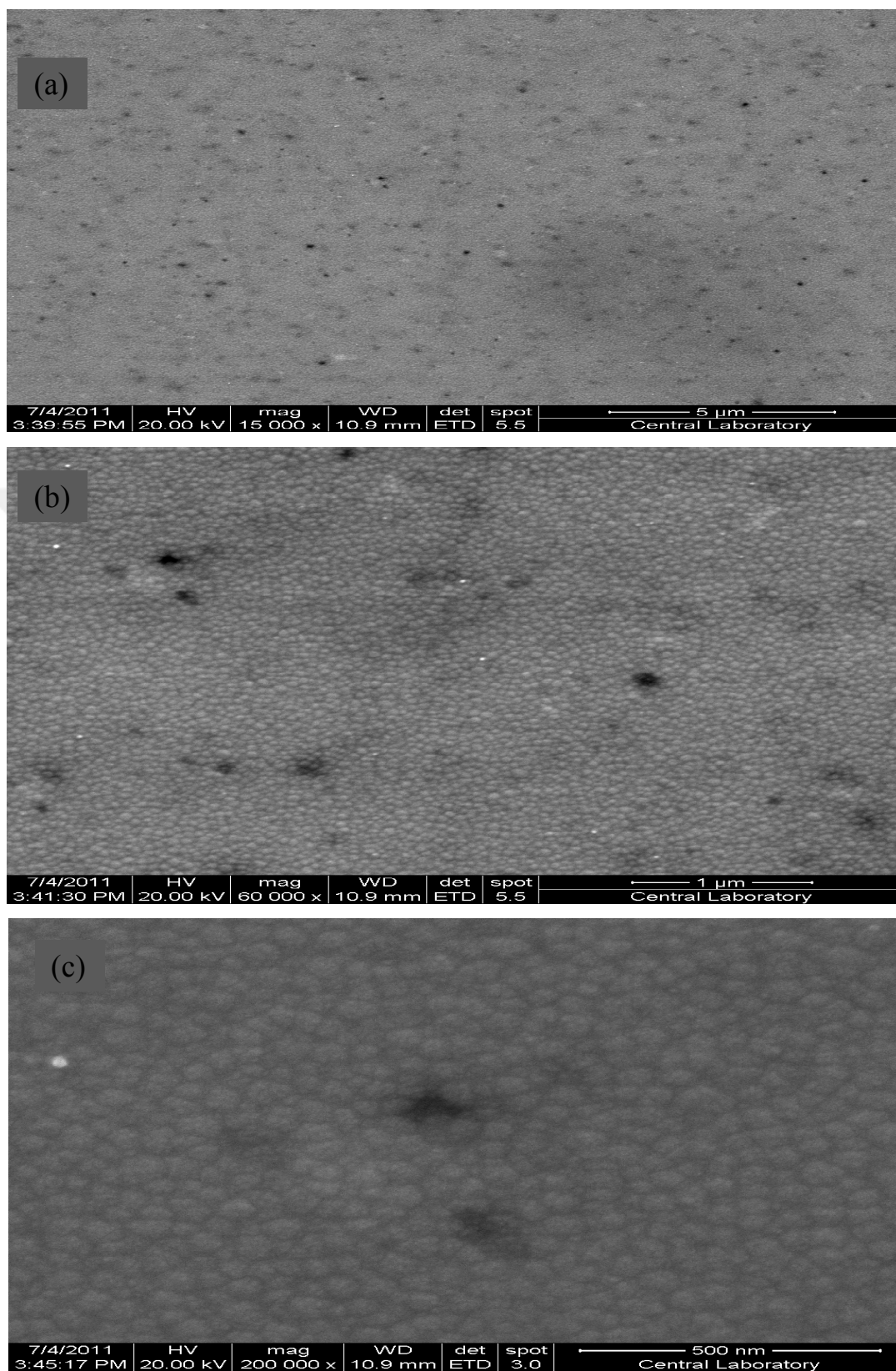


Figure 4.22: SEM image of the samples deposited at substrate temperature of 400°C and annealed 450°C, images 5 μ m, 1 μ m and 500nm respectively.

4.1.4. Atomic Force Microscopy (AFM)

The Atomic Force Microscopy (AFM) can be used to study a wide variety of samples that are plastic, metal, glass, semiconductor, and biological samples such as the walls of cells and bacteria. Atomic Force Microscopy can also run by measuring force between the probe and the sample. The probe usually can be a sharp tip which is a 3-6 μm tall pyramid with 15-40nm end radius. Though the lateral resolution of AFM is low ($\sim 30\text{nm}$) due to the convolution, the vertical resolution can be up to 0.1nm.

In this study, the Atomic Force Microscopy used for imaging CdZnTe thin films deposited at 200-300-400 $^{\circ}\text{C}$ RF sputtering temperature then some of them were annealed under 300-450 $^{\circ}\text{C}$ temperature then their images were analyzed with high-resolution.

The experimentally determined two dimensional high – resolution ($\sim 8.8\text{-}13.4\text{ nm}$) and three dimensional low resolution which are $0.5\mu\text{m}\text{--}0.5\mu\text{m}$ surface morphology of CdZnTe thin films as displayed by AFM were shown in Figures 4.23-4.26. Figures 4.23-4.26 show that the typical surface morphology of the CdZnTe thin films. The imaged area was $5.0\text{*}5.0\mu\text{m} - 1.0\text{*}1.0\mu\text{m}$ and $0.5\text{*}0.5\mu\text{m}$. Granule, Pyramidal, Compact, Cavitations free growth of grain size 0-1 μm crystallites can be seen obviously across the surface from the figures. The surface morphology of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films was found to be dependent on the concentration of Zn ions in the electroplating bath. Pyramidal grain growth with compact, void free and nearly uniform morphology were observed for all $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films.

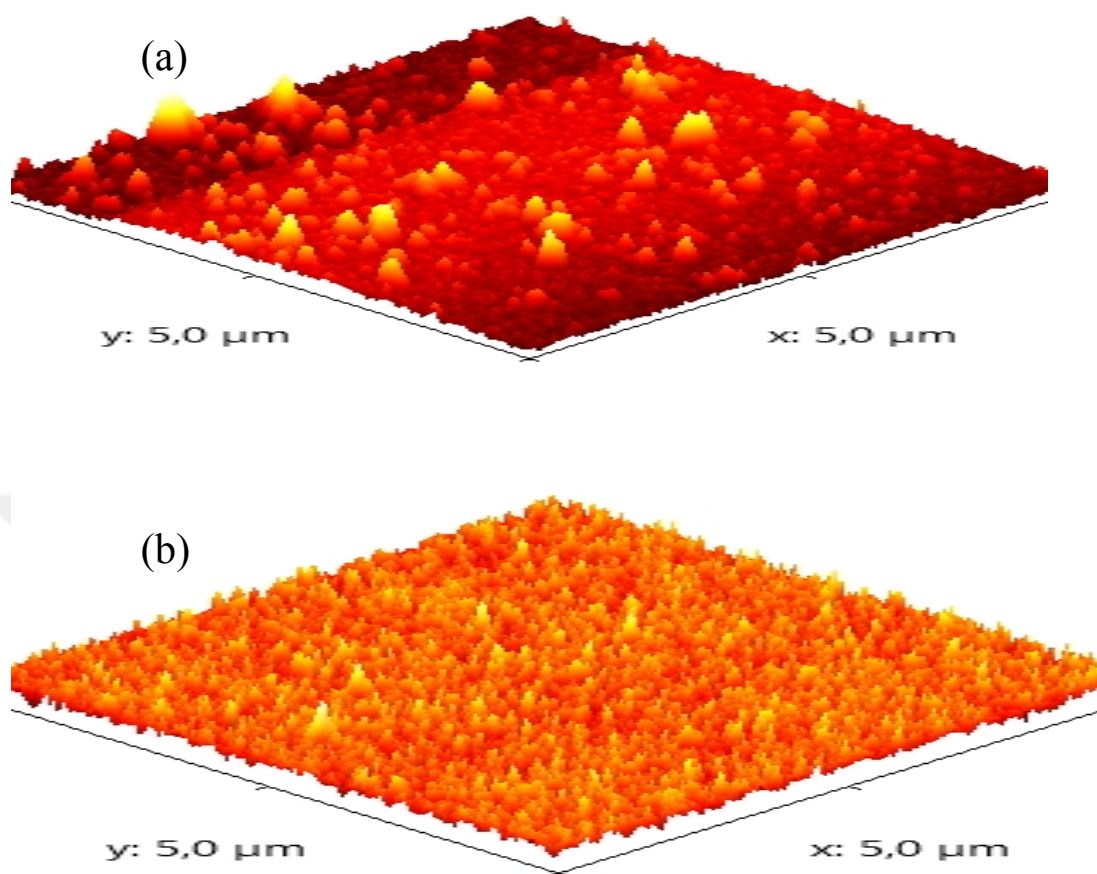
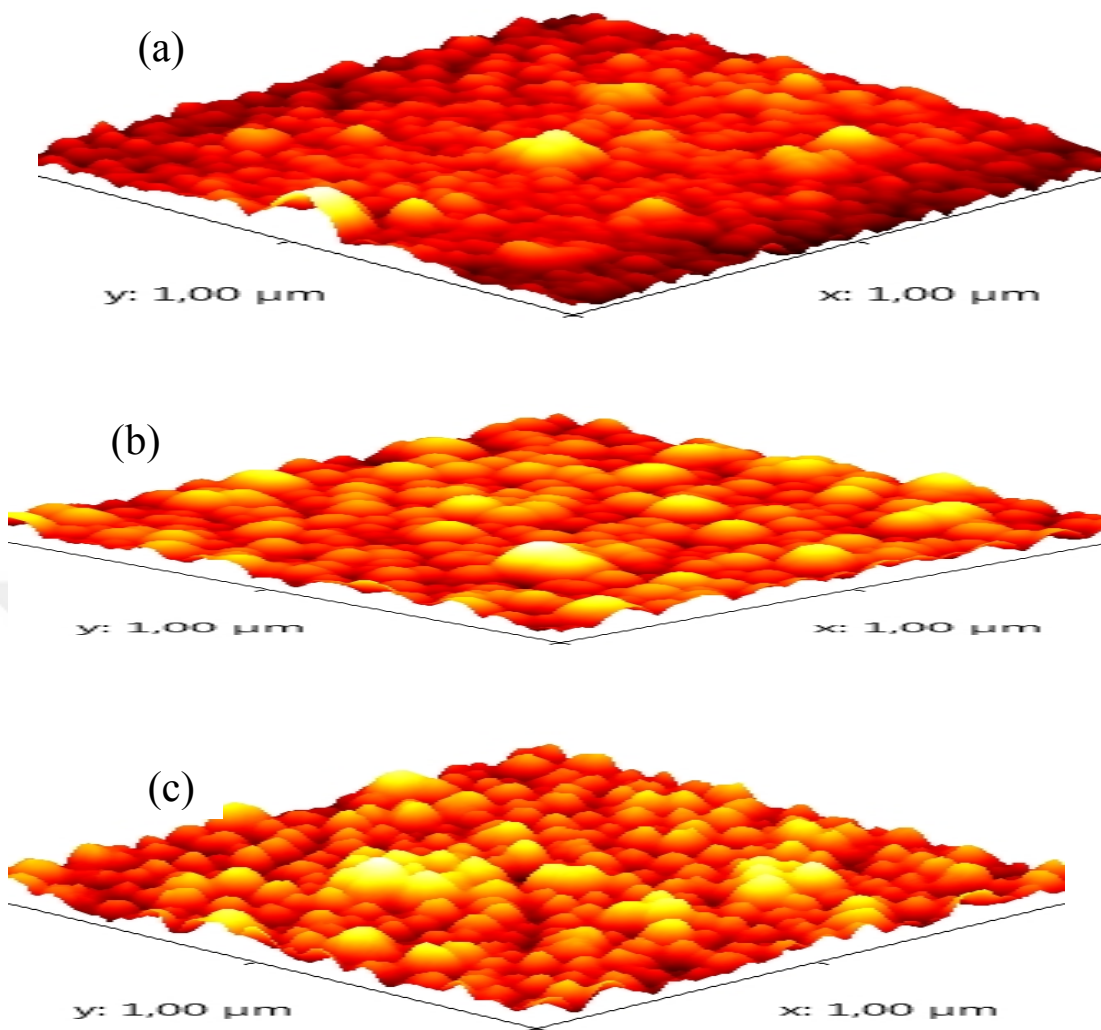


Figure 4.23: AFM images of the samples with $5.0\mu\text{m} \times 5.0\mu\text{m}$ deposited at substrate temperature of a- 200°C and as Grown, b- 400°C and 450°C annealing temp.



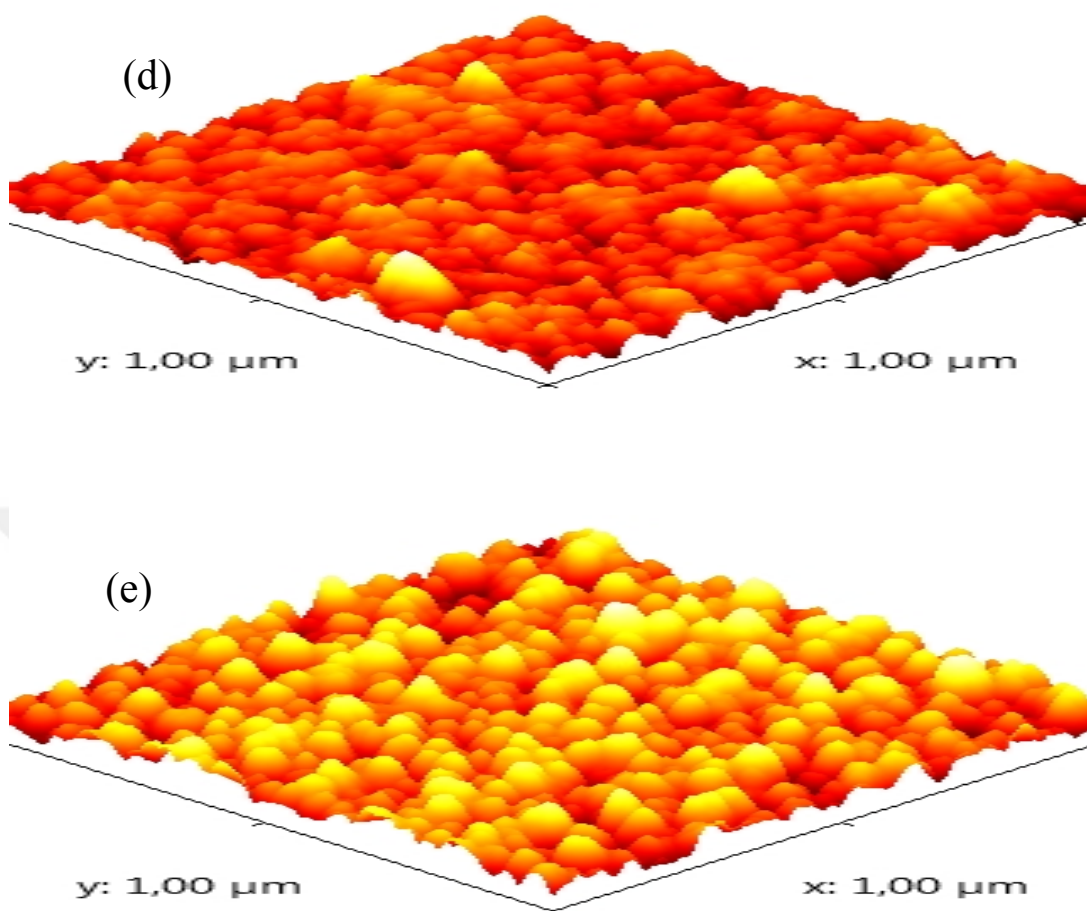
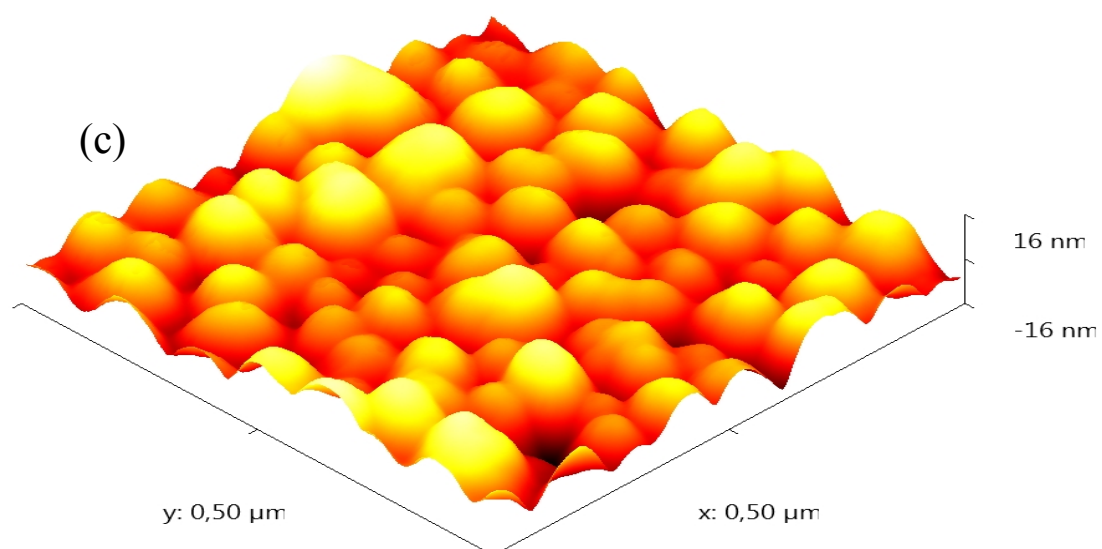
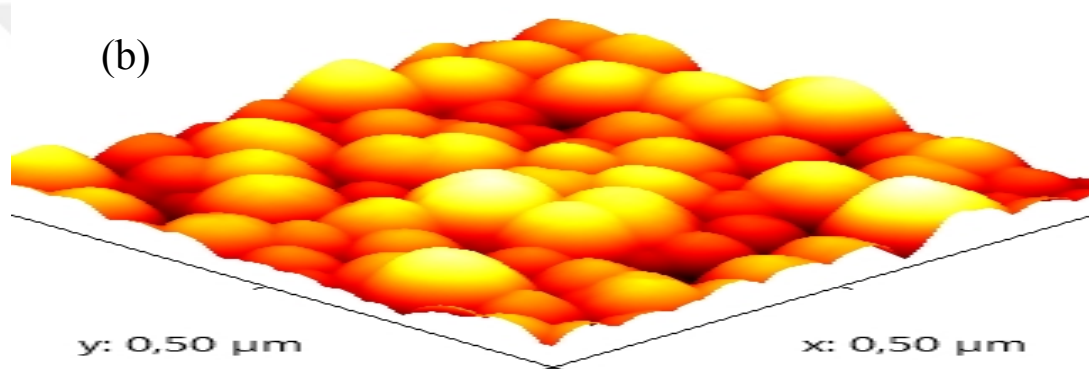
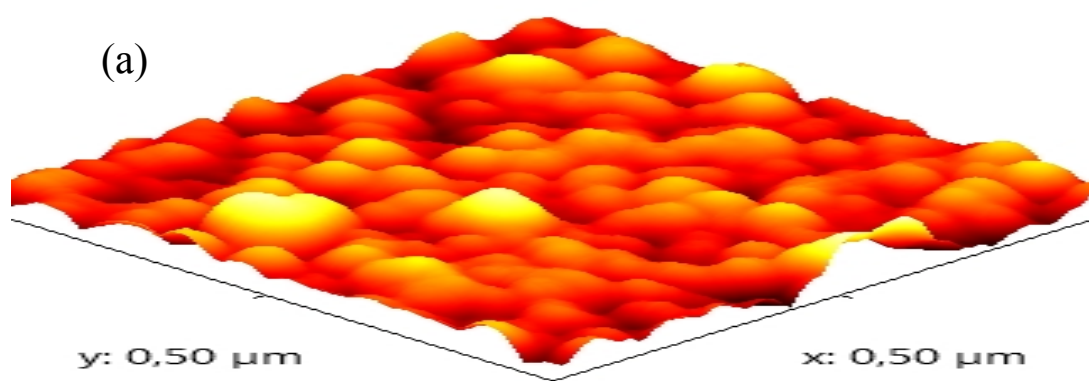


Figure 4.24: AFM images of the samples with $1.0\mu\text{m} \times 1.0\mu\text{m}$ deposited at substrate temperature of a- 200°C and as Grown, (b)- 300°C and as Grown, (c)- 400°C and as Grown, (d)- 400°C and 300 annealing temp.e- 400°C and 450 annealing temperature.



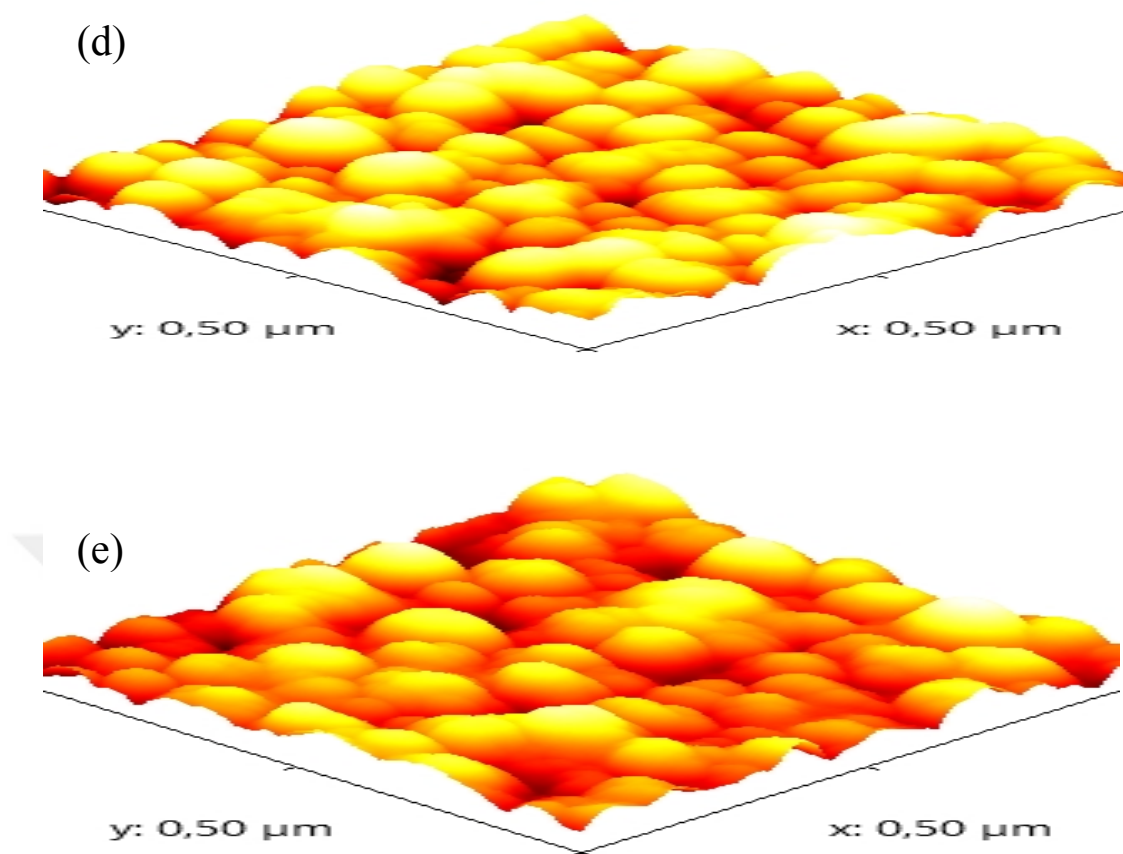
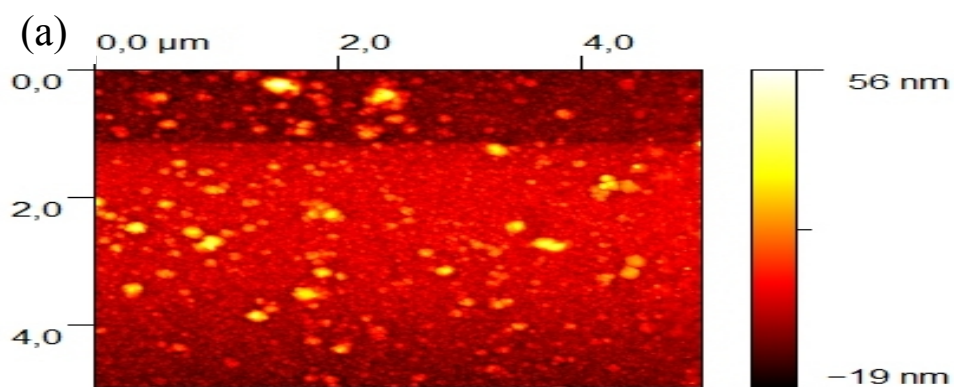
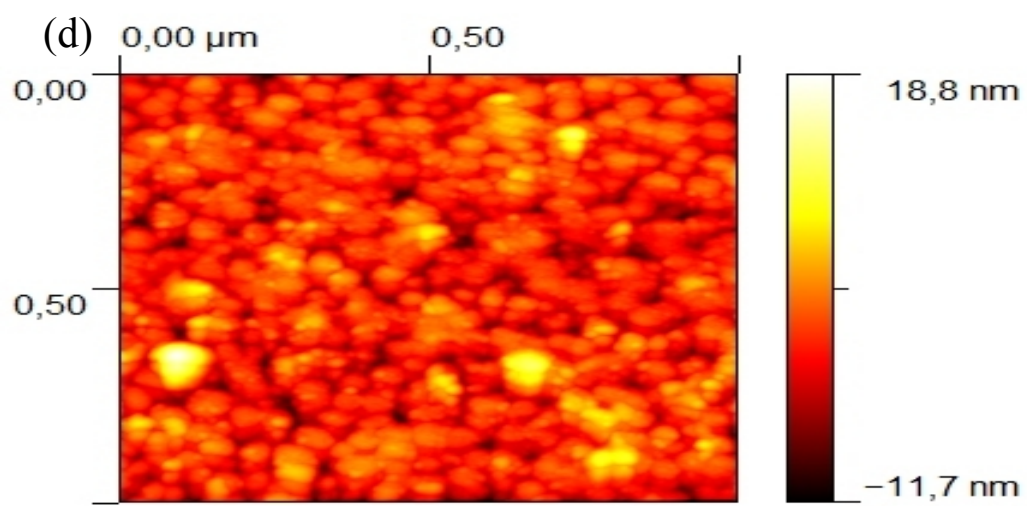
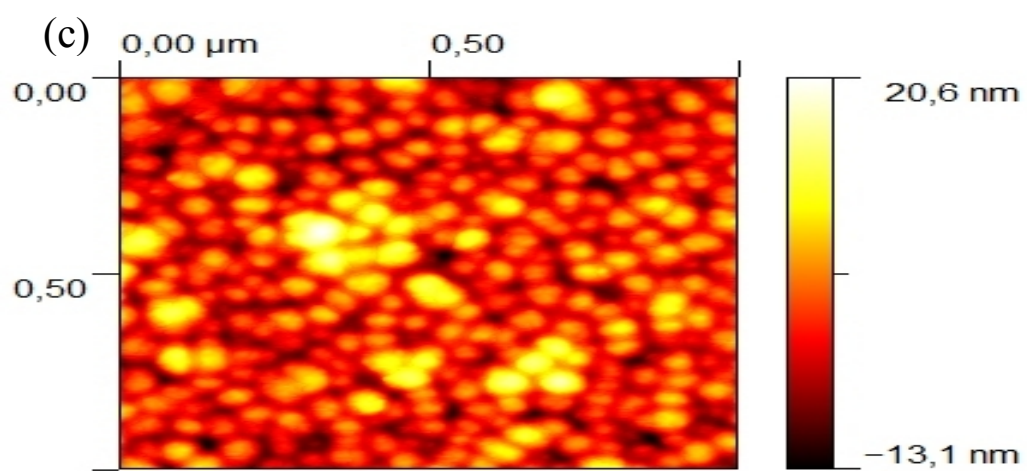
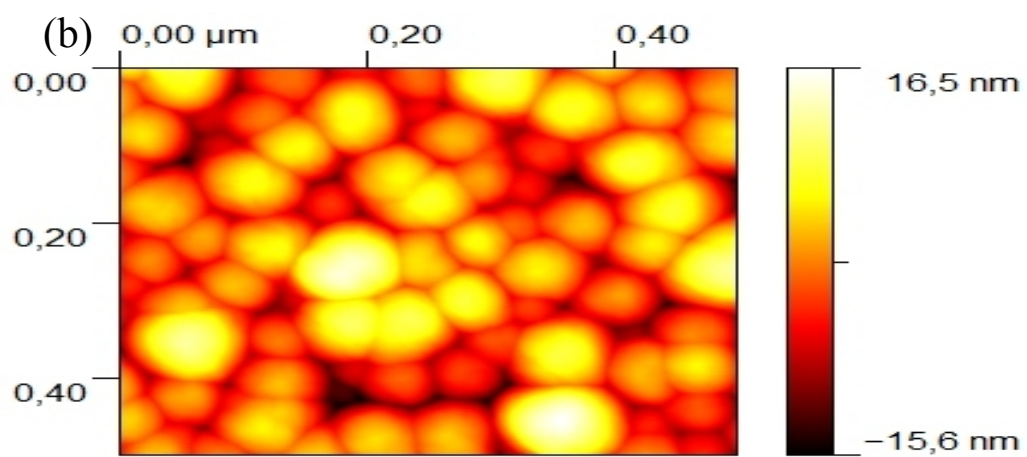


Figure 4.25: AFM images of the samples with $0.5\mu\text{m} \times 0.5\mu\text{m}$ deposited at substrate temperature of (a)- 200°C and as Grown, (b)- 00°C and as Grown, (c)- 400°C and as Grown, (d)- 400°C and 300 annealing temp, (e)- 400°C and 450 annealing temp.





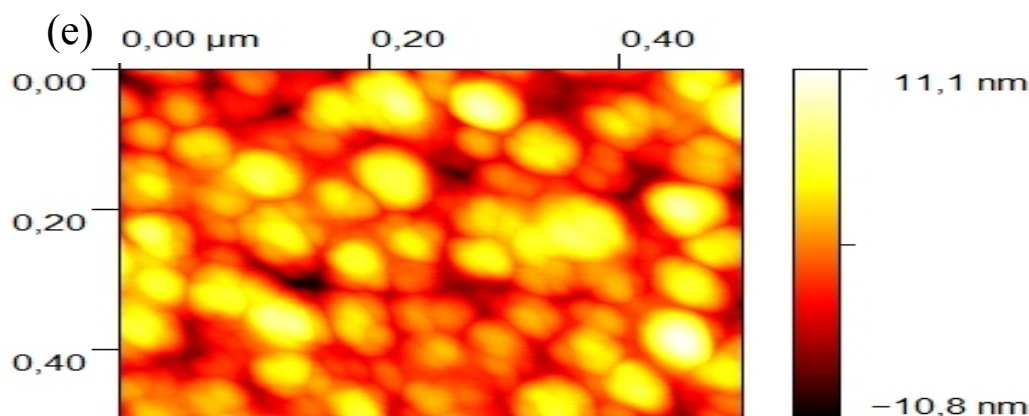


Figure 4.26: AFM images of the samples (a)-deposited at 200°C, as Grown, and images -19;+56nm (b)-deposited at 300°C and as Grown and images from -19;+27nm, (c)-deposited at 400°C as Grown and images from , (d)-400°C and 300 annealing temp, (e)-400°C and 450 annealing temp..

4.1.3 X-ray Photoelectron Spectroscopy (XPS) of Thin CZT

The chemical bonding state and elemental composition of CZT films subjected to different substrate temperature and similar post deposition annealing temperature of as Grown, 300 and 450°C have been analyzed by XPS depth profiling method. This technique enabled us to determine both the stoichiometry and the Zn content of x . The XPS spectra obtained at the initial surfaces of the samples were clearly shown in addition to Cd, Zn and Te. The characteristic peaks of adsorbents; O and C due to the hydrocarbons. The oxygen on surface corresponds to a surface effect because it seems that there is no presence of oxygen in the bulk. The tellurium is relatively little oxidized at the surface. XPS spectra of the films of different compositions deposited at different temperatures indicated the binding energies of the Cd(3d_{5/2} and 3d_{3/2}), Zn(2p) and Te(3d_{5/2} and 3d_{3/2}) levels are observed in all cases. The peak energy levels associated with Cd(3d_{5/2} and 3d_{3/2}) appeared at 404.5 and 411.2 eV respectively. The binding energies of the Te(3d_{5/2} and 3d_{3/2}) levels were observed at 572 and 582.6 eV respectively. The 3d peaks of both Cd and Te are doublets reflecting the 3d_{5/2} and 3d_{3/2} spin orbit splitting. It has been shown that the splitting seen in the 3d peak of tellurium is due to the presence of excess tellurium. The binding energy of Zn(2p_{1/2} and 2p_{3/2}) was observed at 1025 eV and 1021.4 eV.

The 'x' values for the samples deposited on glass at 300⁰C, 400⁰C and both annealed at as Grown 300 and 450⁰C are between 0.37-0.52 under 3500 volt, contrarily, under 2500 volt the calculated x values were between 0.37 and 0.91. Further, as the 'x' value increased, the area under the peak for Zn(2p_{3/2}) also increased and the area under the Cd(3d_{5/2}) decreased as shown in Figure 4.28-4.29. Moreover, the binding energies were found to shift towards ZnTe as the Zn content increased. Depth profile measurements indicated uniform distribution of Cd, Zn and Te throughout the thickness of the films. From the results obtained after decomposition of peaks. It appears that for samples with low Zn concentration; the ratio of (Cd+Zn)/Te is practically constant and very close to the unity. Thus, this indicates that the stoichiometry of ternary films is maintained. However, the samples rich in Zn content are impoverished in Te. In fact, we note a slight decrease in tellurium content for these samples; the ratio of (Cd+Zn)/Te are of about 0.89. All these results are in good agreement with those of XRD and EDS.

The XPS measurements were performed. for five samples deposited at 200-300⁰C and 400⁰C and both annealed at 0-300-450⁰C in the N₂ atmosphere, by an XPS system in the XPS experiments. The surface layers of the samples were successively removed by Ar sputtering and measured again for depth profiling, 20 cyclic measurements were obtained.

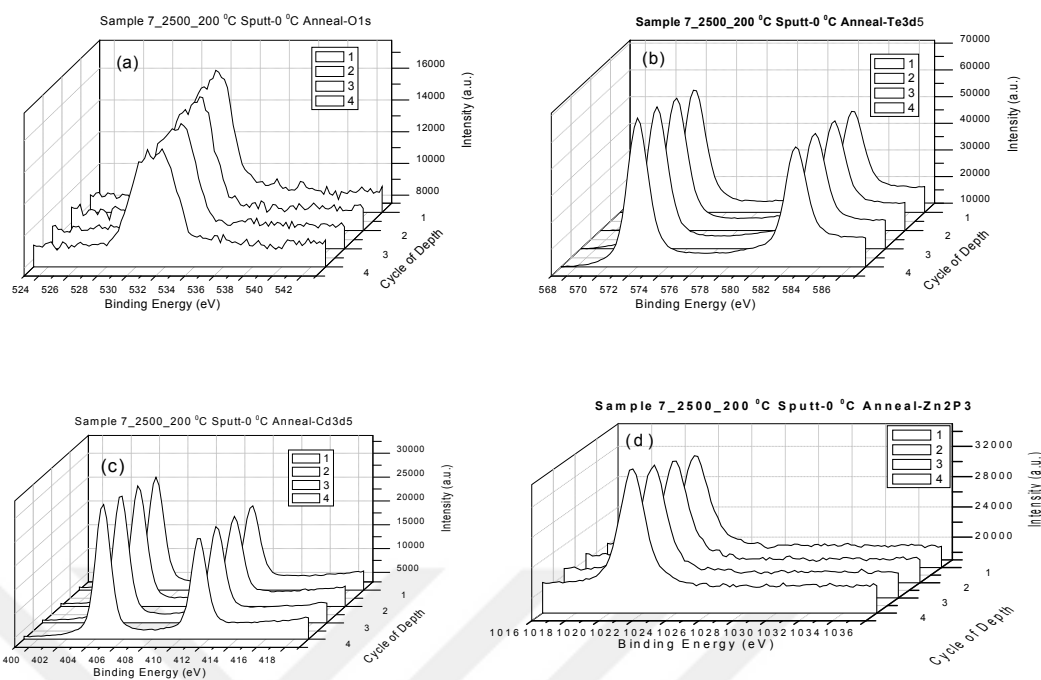


Figure 4.27: XPS spectra of (a)- O1s. (b)- Te3d5.(c)- Zn2p3.(d)- Cd 3d5 respectively electron in the CdZnTe film deposited on glass at 200 $^{\circ}$ C and annealed at as Grown for 4 spectra.

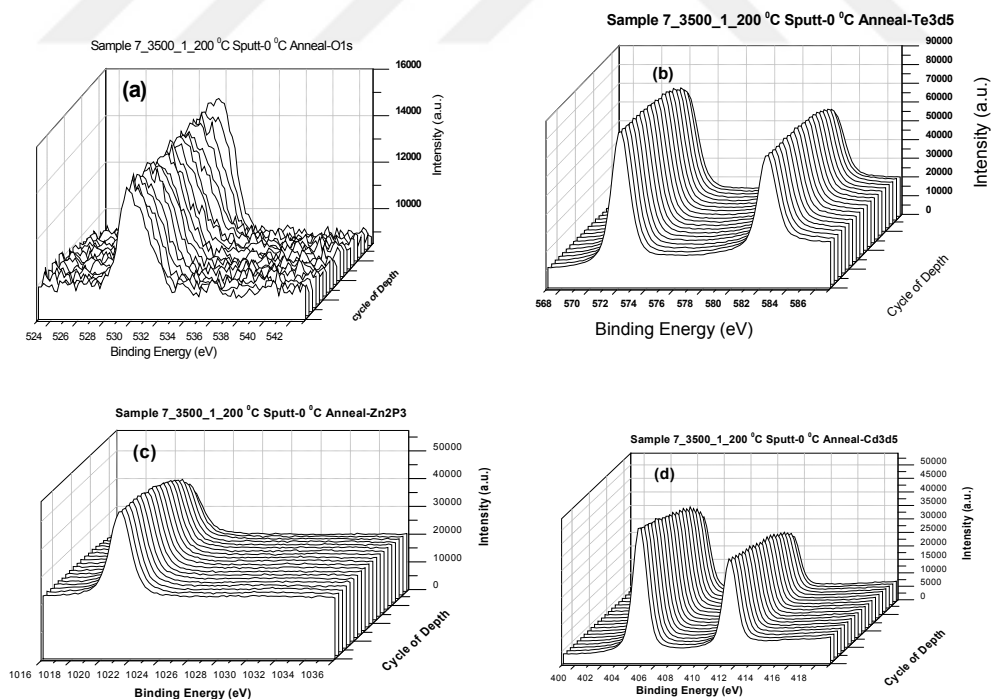


Figure 4.28. XPS spectra of (a)- O1s,(b)- Te3d5,(c)- Zn2p3,(d)- Cd 3d5 respectively electron in the CdZnTe film deposited on glass at 200 $^{\circ}$ C and as Grown for 25spectra.

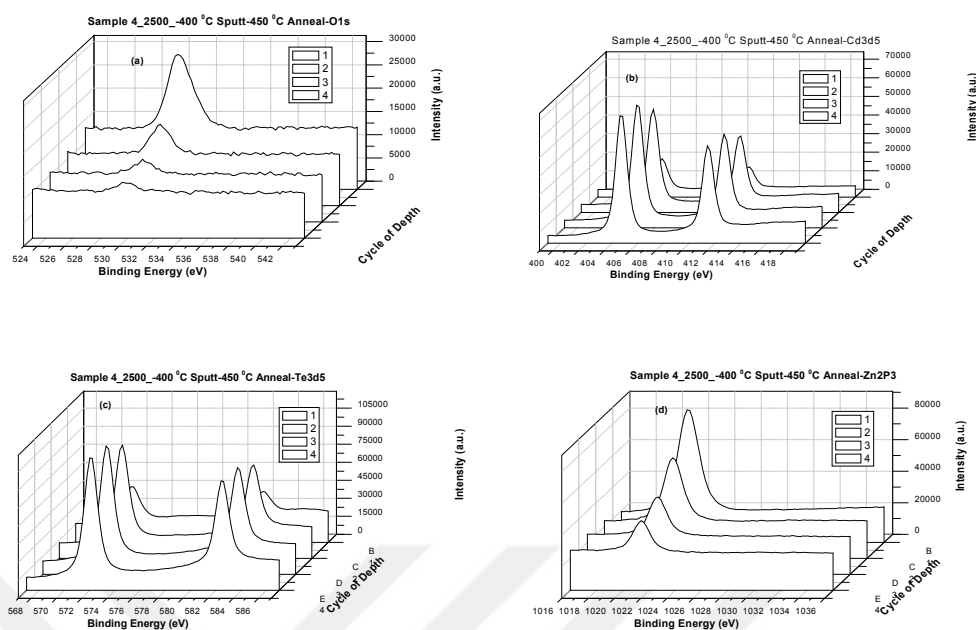


Figure 4.28. XPS spectra of (a)- O1s,(b)- Te3d5,(c)- Zn2p3,(d)- Cd 3d5 respectively electron in the CdZnTe film deposited on glass at 400 °C and annealed at 450 °C under H_2N_2 only for 4 depth spectra.

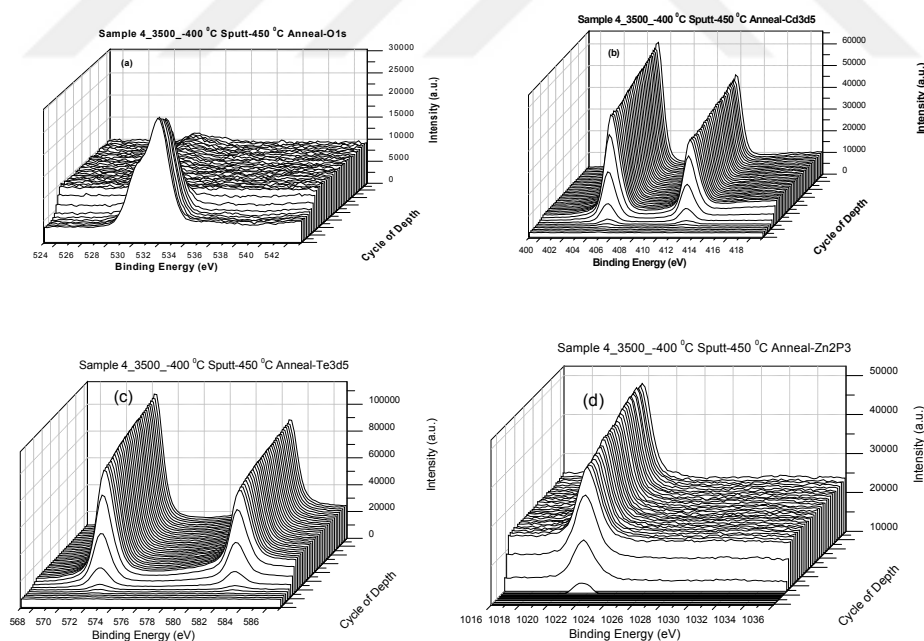


Figure 4.29: XPS spectra of (a)- O1s,(b)- Te3d5,(c)- Zn2p3,(d)- Cd 3d5 respectively electron in the CdZnTe film deposited on glass at 400 °C and annealed at 450 °C.

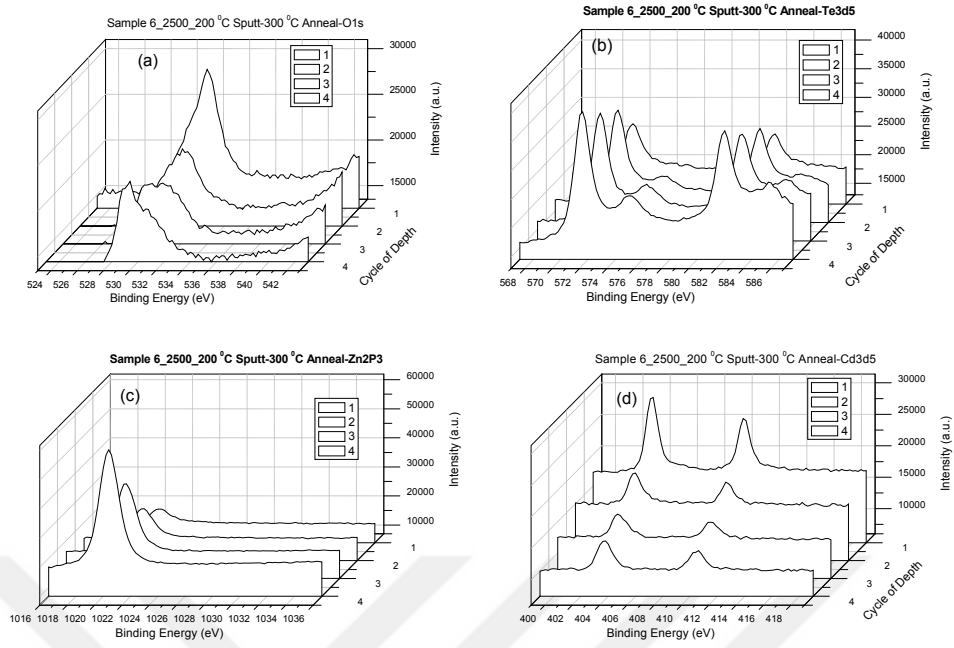


Figure 4.30: XPS spectra of (a)- O1s,(b)- Te3d5,(c)- Zn2p3,(d)- Cd 3d5 respectively electron in the CdZnTe film deposited on glass at 200⁰C and annealed at 300⁰C for 4 spectra.

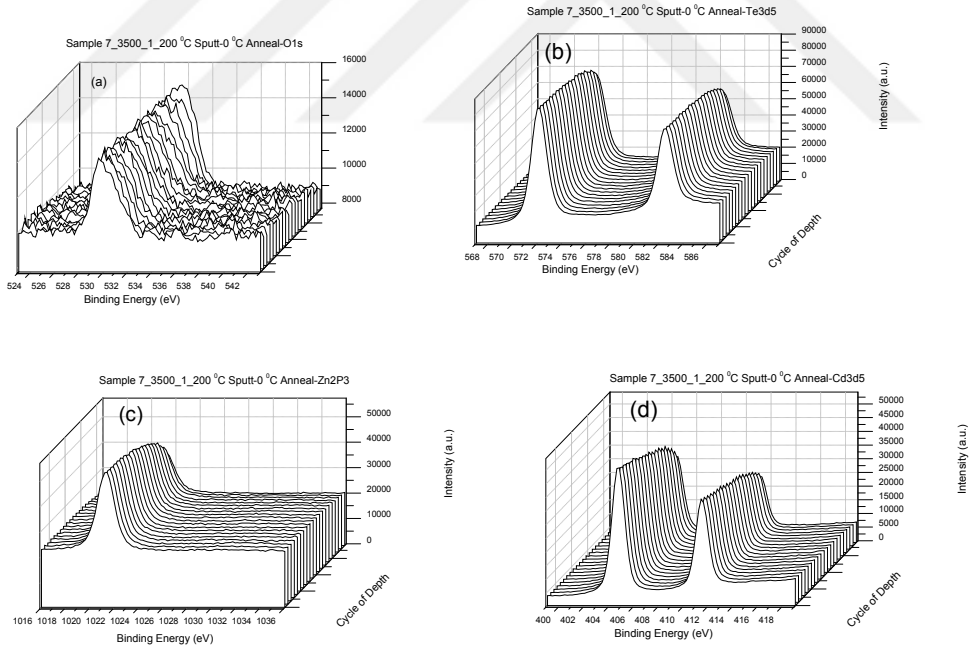


Figure 4.31: XPS spectra of (a)- O1s,(b)- Te3d5,(c)- Zn2p3,(d)- Cd3d5 respectively electron in the CdZnTe film deposited on glass at 200⁰C and annealed at 300⁰C for 25 spectra.

Figure 4.27. Shows the XPS spectra x value can be calculated from the area under Zn2p3 and Cd3d5 from the following formula;

$$x = \frac{Zn}{Zn + Cd} \quad (21)$$

It can be seen from the Figure 4.27 and Figure 4.2.3-a. O1s can be seen on the surface but as the depth becomes larger O1s disappears. This result shows that there is an oxidation on the surface of the sample. Figures 4.27-4.35- b-c-d show Cd-Zn-Te alloy can be found on the glass homogeneously up to a certain depth. After this point of depth the intensity of these alloy decrease and vanish. Consequently it can be said that CdZnTe compound can be found in a certain range and under this depth there is a different compound which is called SiO₂.

Figures 4.32 show 4 spectra of XPS under 2500 volt besides it can be seen from the same figures concentration of the Zn-Cd and Te are uniformed and homogenous at the glass, in spite of that O₁ being at the simple point it couldn't be on the depth of the sample. Figures b-c-d show Cd-Zn-Te alloy can be found on the glass homogeneously up to a certain depth.

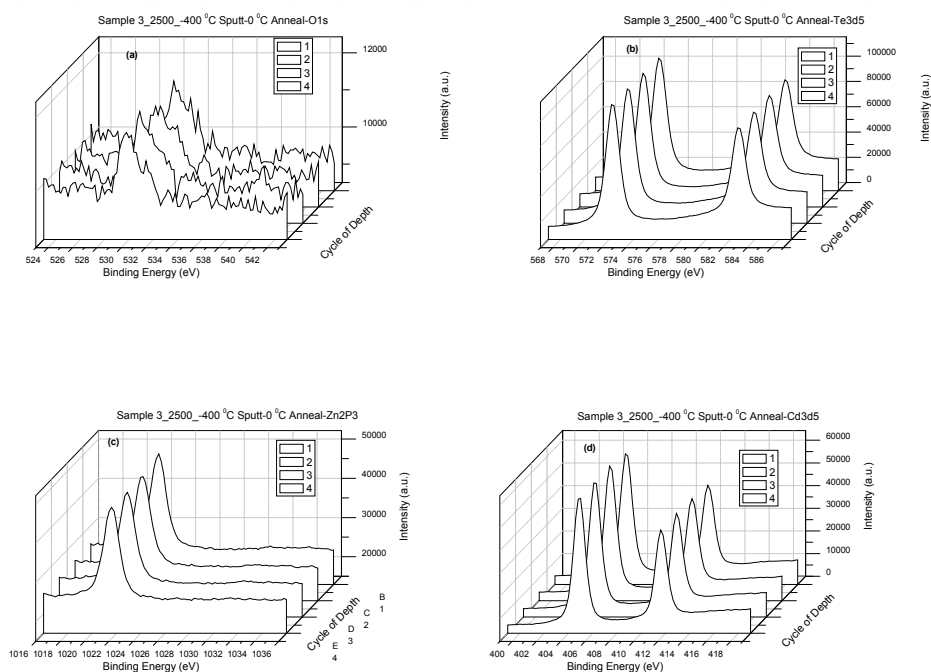


Figure 4.32: XPS spectra of (a)- O1s,(b)- Te3d5,(c)- Zn2p3,(d)- Cd 3d5 respectively electron in the CdZnTe film deposited on glass at 400 °C and annealed as Grown for 4 spectra.

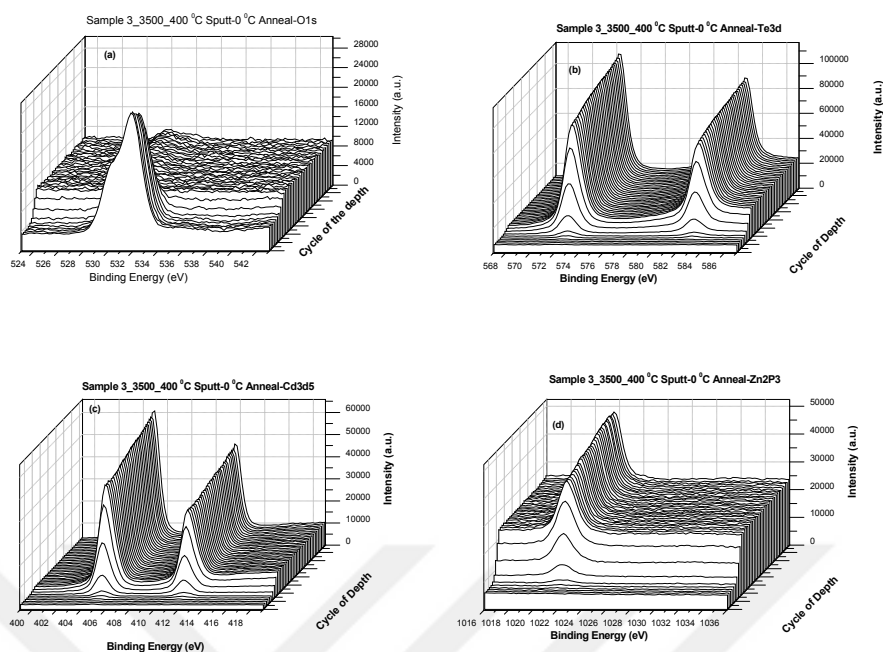


Figure 4.33: XPS spectra of (a)- O1s,(b)- Te3d5,(c)- Zn2p3,(d)- Cd 3d5. respectively electron in the CdZnTe film deposited on glass at 400⁰C and as Grown for 4 spectra.

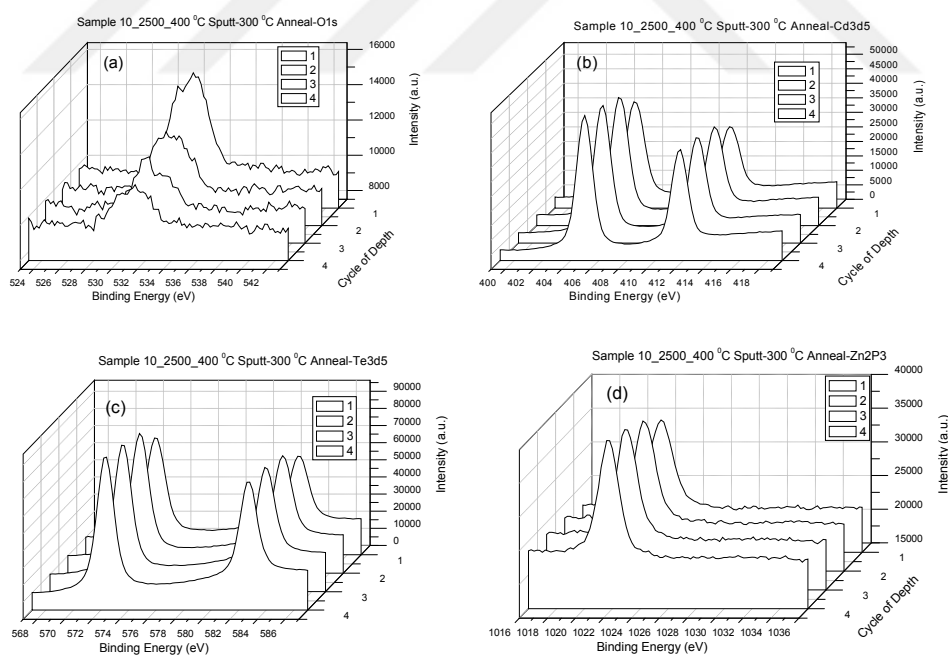


Figure 4.34: XPS spectra of A- O1s . B- Cd3d5. C- Te3d5. D- Zn2p3. respectively electron in the CdZnTe film deposited on glass at 400⁰C and annealed at 300⁰C for only 4 spectra of XPS

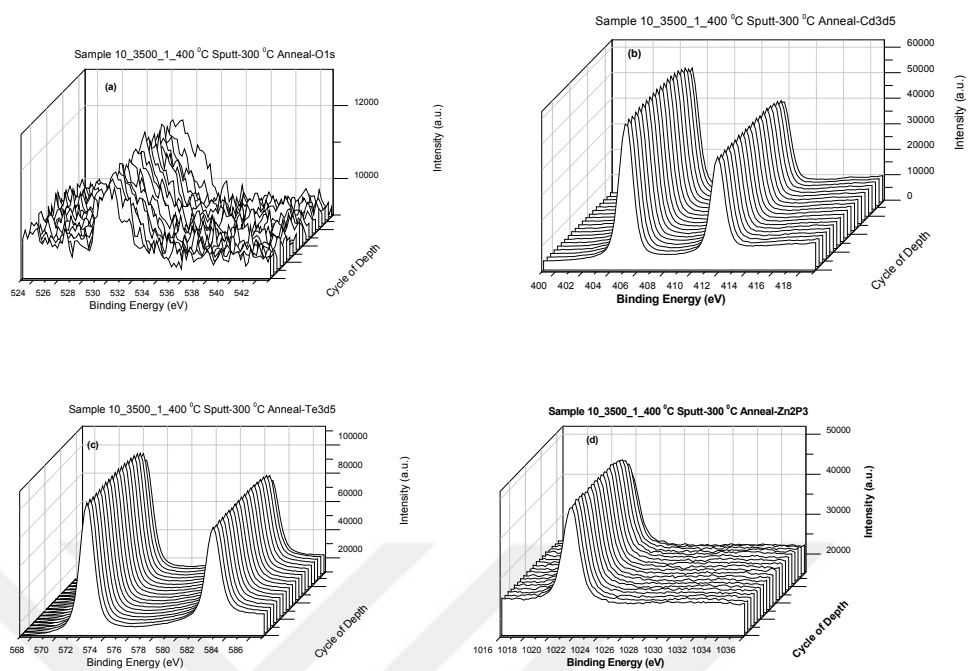


Figure 4.35: XPS spectra of A- O1s, B- Cd 3d5 . C- Te3d5, D- Zn2p3, respectively electron in the CdZnTe film deposited on glass at 400⁰C and annealed at 300⁰C. for 25 spectra of XPS.

Table 5: x value were calculated by using the XPS Peakfit programme from the number of the Cycle of depth by XPS analysis results.

Number of the Cycle of Depth	x= [Zn]/[Zn+ Cd]	Number of the Cycle of Depth	x= [Zn]/[Zn+Cd]
400 RF 0 anneal 2500-3500 volt		200RF-0 anneal 2500-3500 volt	
Cycle 1-2500	0,39	Cycle 1-2500	0,46
Cycle 2-2500	0,37	Cycle 2-2500	0,44
Cycle 3 -2500	0,37	Cycle 3 -2500	0,45
Cycle -2500	0,37	Cycle -2500	0,47
Cycle 4 3500	0,41	Cycle 4 3500	0,51
Cycle 5-3500	0,40	Cycle 5-3500	0,51
Cycle 10-3500	0,40	Cycle 10-3500	0,52
Cycle 15-3500	0,37	Cycle 15-3500	0,52
Cycle 20-3500	0,37	Cycle 20-3500	0,51
400 RF_450 anneal 2500-3500 volt		400 RF-300 anneal 2500-3500 volt	
Cycle 1-2500	0,88	Cycle 1-2500	0,37
Cycle 2-2500	0,59	Cycle 2-2500	0,36
Cycle 3 -2500	0,39	Cycle 3 -2500	0,35
Cycle -2500	0,39	Cycle -2500	0,34
Cycle 4 3500	0,41	Cycle 4 3500	0,38
Cycle 5-3500	0,40	Cycle 5-3500	0,39
Cycle 10-3500	0,39	Cycle 10-3500	0,39
Cycle 15-3500	0,37	Cycle 15-3500	0,40
Cycle 20-3500	0,39	Cycle 20-3500	0,40
200 RF_300 anneal 2500-3500 volt			
Cycle 1-2500	0,39		
Cycle 2-2500	0,76		
Cycle 3 -2500	0,93		
Cycle -2500	0,91		
Cycle 4 3500	0,40		
Cycle 5-3500	0,40		
Cycle 10-3500	0,39		
Cycle 15-3500	0,39		
Cycle 20-3500	0,69		

4.2. CZT Optical Analysis

4.2.1. Absorption and Transmission Measurements

4.2.1.1. Band gap of the deposited CZT films

The transmission spectra in the region of the optical absorption band edge were measured for as-deposited and heat-treated CdZnTe samples. The optical absorption coefficient (α) was calculated from the transmittance using the following relation $\alpha = (1/d) \ln(100/T)$, where 'T' is the transmittance and 'd' is the thickness of the crystal. As a direct band gap semiconductor, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hv): $(\alpha hv) = A (E_g - hv)^2$, where E_g is the optical band gap of the crystal. and A is a constant.

According to the expression $(\alpha hv) = A (E_g - hv)^2$, it should be possible to fit portions of $\alpha hv = f(hv)$ curves to one or more of the standard dependences, namely $(\alpha hv)^2 = f(hv)$ for allowed direct transitions. $(\alpha hv)^{2/3} = f(hv)$ for forbidden direct transitions, and $(\alpha hv)^{1/2} = f(hv)$ for indirect transitions. The analysis of our experimental results, (Figs. 4.36, 4.37, 4.38) shows that the best fit is obtained for $(\alpha hv)^{1/2} = f(hv)$ curves which have a linear portion. Consequently, these curves have been used for the estimation of the band gap values [83-87]. The optical band gaps have been estimated as in the range 1.55- 2.24 eV. The obtained values of E_g for various sputtering temperatures are listed in Table 4. We see that heating the substrate during the deposition causes the band gap CZT increase slightly.

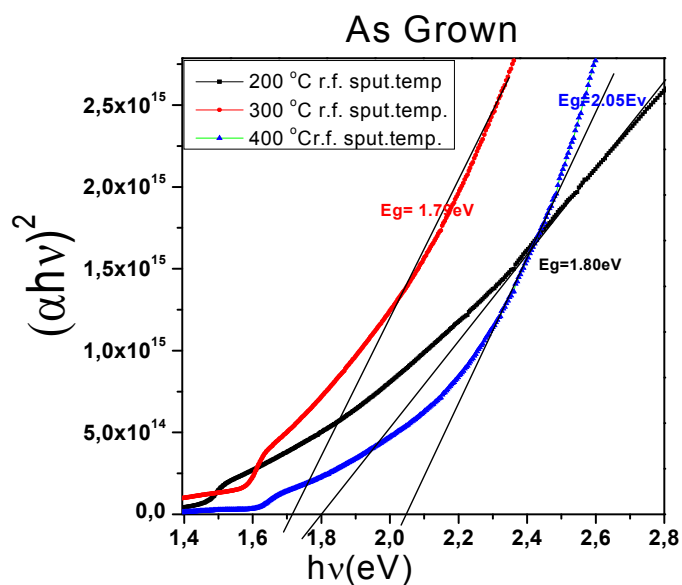


Figure 4.36: UV spectroscopy band gap measurement of CZT thin film Grown at 200-300-400 °C as Grown

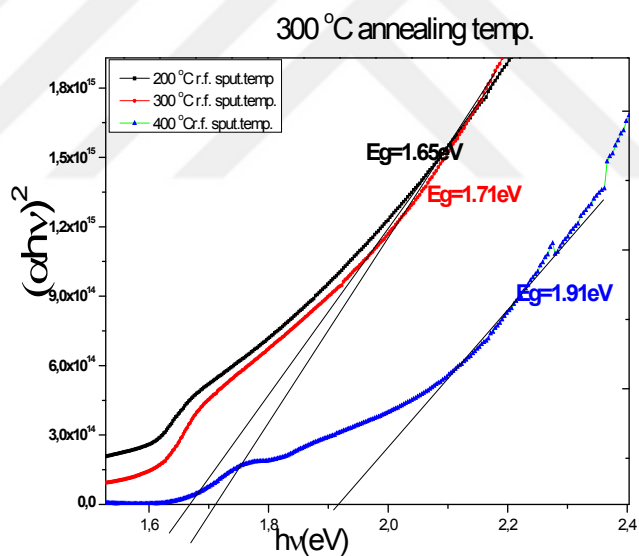


Figure 4.37: UV spectroscopy band gap measurement of CZT thin film Grown at 200-300-400 °C under 300 °C annealing temperature

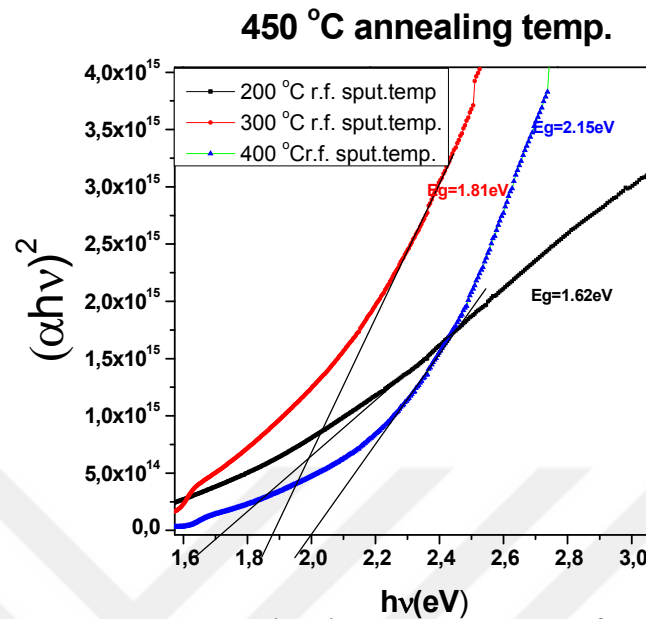


Figure 4.38: UV spectroscopy band gap measurement of CZT thin film Grown at 200-300-400 °C under 450 °C. Annealing temperature.

Figure 4.36-4.38 shows the bandgap calculation from the UV spectroscopy measurement of CdZnTe. It can be seen clearly from the figures that the band gap generally increases with the increase of RF sputtering temperature proportionally.

Table 6. CdZnTe Thin films bandgap values Calculated annealing under N₂ gases

RF temperature °C	Annealing temperature °C	x by E _g	E _g From figure eV (Indirect bandgap)	E _g calculated from eV (1.5045+0.631*X+0.128*X ²)	E _g calculated from eV 1.5+0.76X
200	As Grown	0.46	1.82	1.78	1.81
	300	0.50	1.85	1.60	1.61
	450	0.22	1.65	1.53	1.53
300	As Grown	0.43	1.80	1.78	1.80
	300	0.93	2.20	1.65	1.67
	450	0.43	1.80	1.65	1.67
450	As Grown	0.87	2.15	1.78	1.80
	300	0.97	2.24	1.78	1.80
	450	0.81	2.10	1.65	1.67

Table 7. x values from all measurements

RF sputtering temperature °C	Annealing temperature °C	x value from EDXA	x value from XRD	x value from XPS	x by E _g	E _g from transmission
200	0	0.45	0.32	0.51	0.44	1.80
	300	0.45	0.30	0.40	0.50	1.85
	450	0.50	0.12		0.22	1.65
300	0	0.50	0.30		0.41	1.78
	300	0.43	0.31		0.93	2.20
	450	0.48	0.27	0.39	0.43	1.80
400	0	0.42	0.35	0.37	0.68	2.01
	300	0.40	0.46	0.39	0.97	2.24
	450	0.49	0.43	0.40	0.81	2.10

CHAPTER 5

CONCLUSION

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin films were deposited in vacuum environment with onto heated glass substrates using sputtering method. By deposition of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, nanolayered $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ structures with uniform content at about 200 nm were obtained. By varying the preparation conditions homogenous $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin films can be obtained. Depending on preparation conditions and heat treatment, the optical band gap of respective films can be tuned from 1.70 to 2.24 eV. Results show that $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin film sputtered at 400°C and annealed at 450°C under the N_2 ambient indicated the best behavior. Further works in this area are on the way to improve the performance of the film and its applications in photovoltaic and imaging devices.

In order to characterize CdZnTe thin films, X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray EDS-EDX, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-ray Diffraction Technique (XRD) techniques were used.

The investigation of composition and chemical bonding on the surface and near to the surface of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin films have been studied by performing XPS measurements. XPS was used for enabling us to determine both the stoichiometry and the Zn content of x . The XPS spectra obtained at the initial surfaces of the samples; clearly show in addition to Cd, Zn and Te. The 'x' values for the samples deposited on glass at 200°C , 300°C , 400°C and both annealed at $0-300-450^\circ\text{C}$, x was calculated from ($x = [\text{Zn}] / ([\text{Zn}] + [\text{Cd}])$) formulation and found while deposited 200°C

as Grown was 0.50, other sample deposited 200⁰C then annealed at 300⁰C was 0.40, and the other deposited at 400⁰C, and annealed at 0-300-450⁰C, x calculated 0.39, 0.37, 0.40 respectively. Further, as the ' x ' value increased, the area under the peak for Zn(2p_{3/2}) also increased and the area under the Cd(3d_{5/2}) decreased. Moreover, the binding energies were found to shift towards ZnTe as the Zn content increased. Depth profile measurements indicated uniform distribution of Cd, Zn and Te throughout the thickness of the films. According to the results obtained after decomposition of peaks, it appears that for samples with low Zn concentration; the ratio ($x=[\text{Zn}]/([\text{Zn}]+[\text{Cd}])$) is practically constant and very close to the unity. Thus, this indicates that the stoichiometry of ternary films is maintained.

In order to produce a magnified image of the sample using Scanning Electron microscopy, SEM images showed also that post-annealing and deposition temperature has an explicated effect on the modification of the CdZnTe thin film structure and morphology. It can be seen unambiguously that the large accumulation of Te on the surface of the films vanished while the annealing temperature increases, especially at 450⁰C annealing temperature Te was vanished so there are some black hole seen in the SEM images.

The chemical composition of source and deposited CdZnTe thin films were investigated by using energy dispersive X-ray analysis (EDX or EDS) measurements. On the basis of EDXA analysis, it was found that the as Grown films were not stoichiometric, as follows atomic weight of Cd was further than atomic weight of Zn in the composition, which was also substantiated by structural analysis. Notwithstanding atomic percentage of summation of total Cd; Zn and Te were about 45-60%, the rest of the compound were M, O, Na, Au, Mg etc.

With the help of X-ray Diffraction technique lattice parameters were calculated, the phases existing in the structure were identified, crystalline state were brought (crystalline, polycrystalline or amorphous), and also defects were detected. x value calculated under different deposition and annealing temperature by using ICDD database program from using XRD. x value which calculated from XPS while using XPS Peakfit program.

AFM were measured in three dimensions, x , y , and z (normal to the sample surface), thus enabling the presentation of three-dimensional imaged of a sample surface and also can probe the sample. The surface morphology of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films was found to be dependent on the concentration of Zn ions in the electroplating bath. Pyramidal grain growth with compact, void free and nearly uniform morphology was observed for all $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films.

Table 7 summarizes the obtained results and we can compare them with results achieved by XRD measurements. As can be seen. obtained values of x by XRD are smaller than that's of EDS measurements. We think that two main factors are responsible. First one is related to the involved micro strains or local strains on the nano grains (such as compressive stress) which results to the shift of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ XRD diffraction peaks giving raise to different x values. The other factor is related to the formation of other zinc containing phases like ZnO beside $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ phase.

CHAPTER 6

REFERENCES

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CHAPTER 7

APPENDIX



Appendix 1. Vaksis three magnetron DC/RF sputtering system in Physics Department in Middle East Technical University.



Appendix 2. Rigaku Miniflex XRD in Physics Department in Middle East Technical University



Appendix 3: Energy Dispersive X-Ray system in Central Laboratory of Middle East Technical University.



JEOL 7500F-1
scanning electron microscope

Appendix 4: Scanning Electron Microscopy



Appendix 5: XPS System in Central Laboratory of Middle East Technical University