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Thermal Evaporation and microstructure study of CdTe

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Abstract
Thin films of CdTe deposited by thermal evaporation at evaporation rate of 1000Å thickness on Si substrate.Deposited thin filmthickness is optimized with vacuum deposition conditions by comparing film thickness value from in-process quartz crystal(piezoelectric transducer) with stylus operated dektek surface profiler.CdTe film of thickness 1000 Åhasbeen deposited on silicon substrate by vacuum evaporation method. The thin films are characterized and properties of deposited film depend upon the deposition rate, geometrical position of substrate from the source and surface condition of the silicon substrate. X-ray diffraction (XRD) studyshows that CdTe films are polycrystalline with preferential orientation of (111) plane in cubic phase for 1, 5 & 10 Å/sec deposition rates.Energy dispersive X-ray analysis of CdTe films at 1, 5 & 10 Å/sec deposition rates after quantification gives Te/Cd ratio of 0.98, 1.14 and 1.18 respectively. Scanning electron microscopy (SEM)micrographs of CdTeat different magnifications show grain size in the range of 19-25, 21-28 & 17-20 nm for deposition rates of 1, 5 & 10 Å/sec respectively along the grain boundaries. SEM micrograph at deposition rate of 10 Å/sec has smaller size, smooth, void-free and uniformly distributed over the surface of substrate than the other deposition rates.

1. Introduction

CdTe and ZnS are II-VI group semiconductor with a large band gap in the near UV region. A.A. Ibrahim et. al. [1] discussed that ZnTe a member of II-VI semiconductor having large band gap studied with structural and electrical properties for evaporation film. E.E. Khawaja et al.[2] discussed that ZnTe chemical in homogeneity has been examined by varying deposition rate for thermal evaporation process. S. Larramendi et.al.[3] discussed that ZnTe and CdTe can be grown in form of epitaxial and polycrystalline film by isothermal closed sublimation(vacuum deposition). R. R. Singh et.al. [4] Discussed that CdS has also been identified as a passivant layer for HgCdTe (MCT) IR detector & studied its various physical, electrical and optical properties as an alternative to CdTe and ZnS. Thus combination of CdTe & ZnS provides a very large band gap has been proved to be excellent passivant of MCT based IR applications. R. Pal et.al. [5] Stated that CdTe as a passivant studied and analyzed for interface composition for HgCdTe photodector. CdTe & ZnSthin films have been usually deposited by many techniques such as chemical vapor deposition, electrode position, vacuum deposition, molecular beam epitaxial. K. Nagamani et.al [6] stated that ZnSis used in copper indium gallium diselenide (CuInGaSe2)-based solar cells by lowering its resistivity by Al doped chemical bath process. But vacuum deposition is best since it controls the deposition parameter effectively and it is very conventionally stablized process. F. Gode et. al.[7] discussed that ZnS deposited by chemical bath process at 80°C shows hexagonal structure with polycrytalinity with grain size 40-80nm. Physical methods produce the atoms that deposit on the substrate by evaporation and sputtering. Sometimes called vacuum deposition because the process is usually done in an evacuated chamber.PVD is used for metals while dielectrics can be deposited using specialized equipments. It rely on thermal energy supplied to the crucible or boat to evaporate atoms. Evaporated atoms travel through the evacuated space between the source and the sample and stick to the sample. Few, if any, chemical reactions occur due to low pressure can force a reaction by flowing a gas near the crucible. Surface reactions usually occur very rapidly and there is very little rearrangement of the surface atoms after sticking. Thickness uniformity and shadowing by surface topography, and step coverage are issues. Ali Moarrefzadeh et al. [8] discussed that Physical vapor deposition (PVD) includes a wide range of vacuum coating processes in which material is physically taken out from a source by evaporation or sputtering, transported through a vacuum or partial vacuum by the energy of the vapor particles, and condensed as a film on the surfaces of appropriately placed parts or substrates. The dependent parameters are starting composition, oxidation state, and crystalline structure and packing density.PVD techniques used generally are basically two in nature: thermal evaporation by resistively heating or by using an electron- beam heating, and sputtering, a no thermal process. Deposited films are typically evaluated for visual defects, thickness, and adhesion. Visual defects such as bare spots, small voids, incorporated flakes, or debris can be observed with a stereo microscope having a magnification of 10 to 100 times. Film thickness is generally measured by with dektek surface profilometer with diamond size of 12.5µm radius stylus. In thermal evaporation process, load the source material-to-be-deposited (evaporant) into the container (crucible). Then resistively heat the container (tungsten or molybdenum boat) containing source to high temperature i.e. evaporation temperature depending upon the material to be deposited. The source material evaporates and evaporant vapor

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transports to and impinges on the surface of the substrate. Evaporant condenses on and is absorbed by the surface.

Thermal evaporation is very old, easy, reliable and good method of deposition while E-beam evaporation requires elaborate and complex system. Moreover high velocity electron creates surface defects and stress on the deposited surface**.**

2. Literature Review

Vivienne Denise Falcão et.al. [9] discussed that CdTe deposition used in photovoltaic applications by closed space sublimation process depends upon the influence of deposition parameters on the properties of CdTe film. E. R. Shabban et.al. [10] discussed that film thickness influence the microstructure and optical properties . He found that crystallite size increases while microstrain decreases with increasing film thickness. Laxman Gouda et.al. [11} discussed that the properties of CdTe film deposited on glass and ITO coated glass by chemical bath method depends upon the chemical composition of the chemicals used. The atomic ratio in the film is a function of the Cd/Te concentration ratio in the solution used in deposition. A. Romeo et.al. [12] stated that crystallization and morphology of the CdTe is strongly affected not only by the CdCl2 treatment but also by the deposition method and the structure of the CdS windows on the TCO substrates, they also affect the influence of post-deposition treatment on CdTe.M. Estela Calixto et.al. [13] stated that CdTe can be deposited for Cu (In, Ga) Se2 thin film solar cells by close spaced vapor transport technique, named as "CSVT", is a variant of the sublimation technique, it uses two graphite blocks, where independent high electrical currents flow and due to the dissipation effect of the electrical energy by Joule's heat makes the temperature in each graphite block to rise. One of the graphite blocks is named the source &other substrate with inert gas atmosphere. The rate of deposition is controlled by gas flow and pressure. Wagner Anacle to Pinheiro et. al. [14] carried out study on different CdTe source like affecting the deposition rate and found that largest deposition rate was achieved when a paste made of CdTe and propylene glycol was used as the source and compacting the powder the deposition rate increases due to the better thermal contact between powder particles. G. Gordillo et.al. [15] discussed that the interest in studying CdTe & ZnS materials is due to their capability in using photovoltaic solar cells applications and by changing their composition structure changes. J. Wang et.al. [16] Near-Infrared (NIR) fluorescence-based bio-sensor and imaging applications used quantum dots of CdTe/CdS by synthesing microwave-assisted. Osvaldo de Melo et.al. [17] stated that alumina membrance used during vacuum evaporation develops pattern applicable in functional nano-strutures, nano-arrays and organic sensors. K.A.M.H. Siddiquee et al. [18] discussed that CdTe/CdS based solar cell can be developed by chemical bath & electrode position optimized process condition through characterization. Condensation and nucleation- Atoms that impinge on a surface in a vacuum environment may be reflected immediately, re-evaporate after a residence time, or condense on the surface. Mean free path is the minimum distance between two successive collisions. Based on this mean free path source to substrate distance is optimized for constant flux and better deposited film quality. Vapor pressure varies depending upon the source temperature and is different for different materials. Re-evaporation is a function of bonding energy between the adatom and the surface, the surface temperature, and the flux of mobile adatoms e.g. the deposition of cadmium on a steel surface having a temperature greater than about 200 ˚C will result in total re-evaporation of the cadmium. The energy of the atom, atom-surface interaction (chemical bonding), and the temperature of the surface influence the capability of an atom on a surface. The mobility on a surface can change because of variations in chemistry or crystallography. The various crystallographic plates of a surface have different surface free energies that influence the surface diffusion. Atoms condense on a surface by losing energy. They lose energy by: -forming and breaking chemical bonds with the substrate atoms. -Finding preferential nucleation sites (lattice defects, atoms steps, and impurities)- interacting with another diffusing surface atoms (same species) - Colliding or reacting with adsorbed surface species.

Atoms form nuclei after condensation. Homogenous nucleation is said to occur if the surface is of same material as the deposition atoms and if they are different materials, the process is called heterogeneous. In semiconductor field, heterogeneous nucleation forms hetero- junctions.

3. Experimental Set-Up

The island films were prepared using a laboratory thermal evaporation setup working at residual vacuum of (2.5 - 4) $\times 10^{-6}$ mbar. The deposition setup was equipped with the two-stage vacuum system based on turbo molecular along with. In case of oil based pumps the ultimate vacuum achieved in the system depends upon the vapor pressure of the oil used in pumps, generally Silicone based oils are used to achieve vacuum of1.0×10^{-6} mbar order in the chamber. The films were deposited on the substrates cleaned in the ultrasound bath in isopropyl alcohol and drained by a compressed air flux. High purity 99.999% CdTe small chunks (pieces) used as source material with open type molybdenum boats. During the deposition, all substrates were kept at room temperature i.e no substrate heating or cooling.

In this case, certain assumptions about the structure of the film, the shape and size of the islands, can be made only on the basis of measurement of electrical and optical

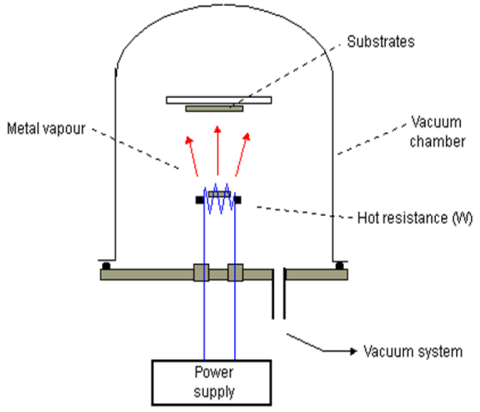

Fig: 1. Mechanism of Thermal evaporation process (ref. [8])

properties of this film and topographic surveillance using SEM or AFM. Optical absorption and transmittance of CdTe films on glass substrates were measured in wavelength range from 200 to 1100 nm using the 640FT IR spectrometer. Flow regimes are categorized quantitatively via the Knudsen number (Kn), which represents the ratio of the molecular mean free path to the flow geometry size for gases. Generally, the ambient temperature is fixed based on the experimental setup or experimental conditions but the evaporation temperature can be varied as per the thickness or mass transfer to be deposited on the substrate. This evaporation temperature can be increased or decreased depending considering the vapour pressure, to make fast the mass transfer keeping the good adhesion with uniformity on the substrate surface.

4. Results and Discussion

In table 1 various input parameters required for computing the depositing film thickness during the thermal evaporation process of different source material like CdTe in our case by a piezoelectric transducer using quartz crystal are given.

Table 1: Input parameters for Digital Thickness Monitor (DTM)

Name of material	Density (g/cm^3)	Acoustic Impedance Value	Tooling factor
CdTe	4.85	9.01	100
ZnS	8.85	11.39	100
Tin	7.30	100.00 Pa	100
Indium	7.31	0.11871kg/mol	100
Gold	7.36 g/cm^3	7.36E3 kg/m³	100

Generally the deposited film thickness value does not match with the value given by DTM. So, we measure the deposited film thickness at different points on the substrate surface from Dektek surface profiler which are shown in figure 2. Generally, the variation in thickness value from DTM is 5-15%. So, we have to keep the DTM thickness value such that the actual value measured from Dektek matches with required thickness value. This can be achieved by doing a no of repetitive experiments and reducing gap between substrate and quartz crystal.

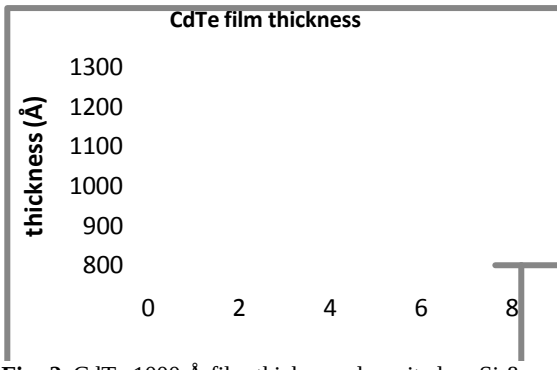

Fig: 2. CdTe 1000 Å film thickness deposited on Si & measured at different points on Si substrate surface

The film thickness may vary by varying the evaporation temperature with time and vapor pressurefrom the centre of substrate to outer surface and it is maximum at the centre as definitely there is loss of source material during thermal evaporation since only a fraction of the material is deposited on the surface while we are evaporating a large quantity of it.

4.1 XRD Results

Figure 3(a), 3(b), 3(c) shows the XRD patternby using Kα (wavelength 1.541874) of CdTe on silicon with deposition rate of 1, 5 & 10 Å/sec. Several well defined peaks are observed in the XRD pattern. The XRD analysis reveals that the films are polycrystalline, and the sharp peaks are identified as (111), (220), and (311) planes of CdTe. The strong peak at 23.76° corresponds to the reflection of cubic (111) plane for all the deposition rates. No diffraction peaks associated with metallic Cd, Te or other compounds were observed. This shows that respective layered structures present a single phase with highly oriented CdTe crystallites with the (111) planes parallel to the substrated. The nature of substrate on which CdTe is deposited influence the grain orientation in the film. The low intensity peaks observed in XRD pattern shows that the films are coarsely fine crystallites or nano-crystalline. The broad hump in the displayed pattern is due to the Si substrate and also possibly due to some amorphous phases present in the CdTe thin films as shown in figure 3(a). The intensity of the peaks of 1A/sec is stronger than other deposition rates indicates the improvement of crystalline quality. The Strong and sharp peak diffraction peaks indicate the formation of well crystalline film. It shows that the major peak (111) is strongly dominating the other peaks as shown in fig 3(a), (b), (c)). Figure 3(d) shows the XRD of polished silicon used as reference for comparing the depositing CdTe film of different thickness at different deposition rate. Thus from these XRD results it shows that fcc structure for fixed thickness of CdTe is independent of deposition rates.

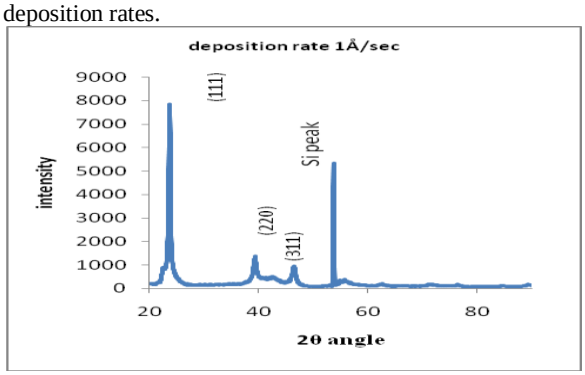

Fig: 3(a) CdTe deposition on Si at deposition rate of 1Å/sec

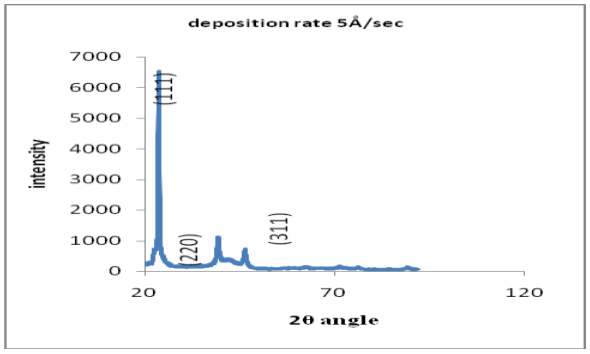

Fig: 3(b) CdTe deposition on Si at deposition rate of 5Å/sec

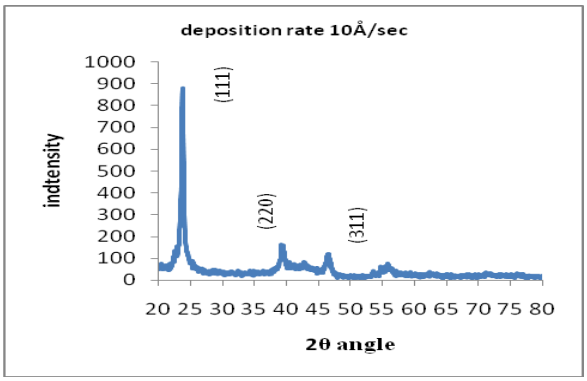

Fig: 3(c). CdTe deposition on Si at deposition rate of 10Å/sec

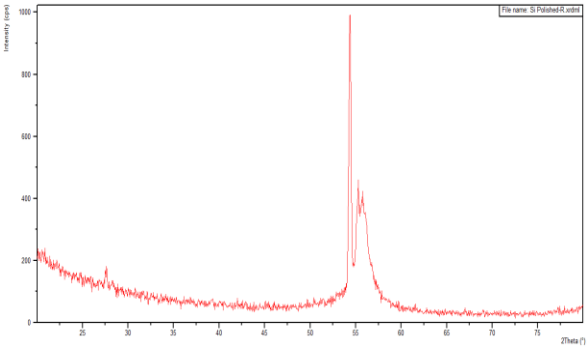

Fig: 3(d). XRD Analysis of Polished Silicon

4.2 EDX Results

Energy dispersive X-ray (EDX) analysis indicated the presence of Cd and Te for all the deposited layers as shown in figure 4. The average atomic ratio of Te/Cd, calculated from the quantification of the peaks, gives the values of 0.98, 1.14 and 1.18 for different deposition rates 1, 5 & 10Å/sec respectively. Also the atomic percentage of Te increases while Cd decreases with increasing deposition rates as shown in table no.2. These results indicate that the average atomic ratio of Te/Cd increases with decreasing deposition rate, ratios of the films are not matching with the stoichiometric ratio (Te/Cd =1) and the surface of the sample is rich in metal. Deviation from the atomic percentages of Te/Cd ratios could be attributed to the presence of higher atomic percentage of oxygen revealed from the EDX of the films.

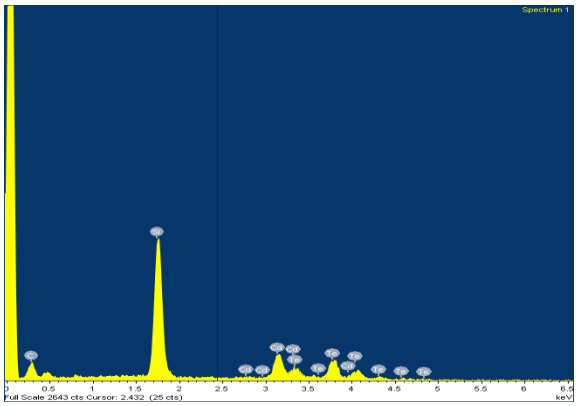

Fig: 4. EDX Scanning Pattern of CdTe on silicon

Oxygen or other impurities may be incorporated in the film either from the atmosphere or from the outgassing from chamber walls etc. Atomic percentage of oxygen or other impurities increases with the increase in deposition rates. EDX analysis of CdTe thin films with different deposition rates are listed in Table 2

Table: 2. EDX Analysis of CdTe with Different Deposition Rates

Deposition rate	Atomic %			Wt.%	
	Te	Cd	Te/Cd ratio	Te	Cd
1Å/sec rate	49.94	50.06	0.98	53.11	46.89
5Å/sec rate	53.47	46.53	1.149	56.61	43.39
10Å/sec rate	54.16	45.84	1.18	57.28	42.72

4.3 SEM Results

Figure 5(a), 5(b), 6(a), 6(b) &7(a), 7(b) shows the SEM micrographs of CdTe 1000 Å thin film with 1, 5 &10 Å/sec deposition rates on silicon substrate respectively at 50KX &100KX magnifications, 5KVEHT, for study the microstructure and grain size.

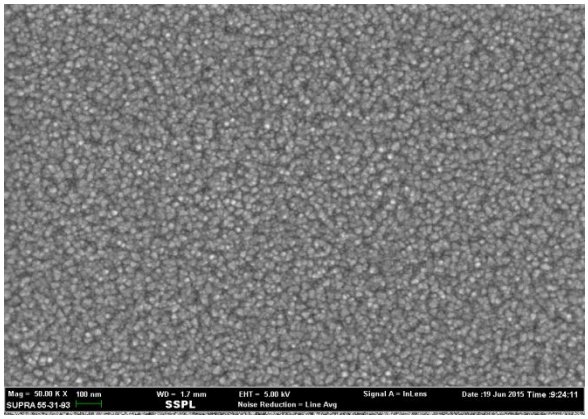

Fig: 5(a). SEM micrographs of CdTe at 50KX magnification with 5KV at deposition rate of 1 Å/sec

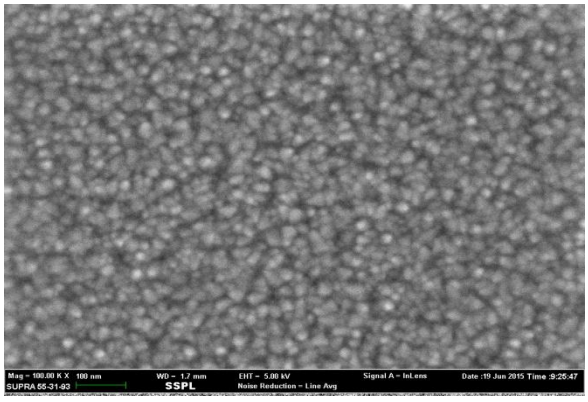

Fig: 5(b). SEM micrographs of CdTe at 100KX magnification with 5KV at deposition rate of 1 Å/sec

The SEM micrographs show that the Si substrate is deposited with CdTe without cracks and pin-holes and is well covered. In case of deposition rate of 10 Å/sec, the grain size is very small and more evenly distributed. The grain size is in the range of 17-20 nm. The 20 nm grain size

grains are very few which means most of them are below 20 nm size as shown in figure 6(a),6(b).The SEM micrographs of.deposition rate of 1 Å/sec as shown in figure 4(a),4(b), also shows the good uniformity with grain size of 19-25 nm but not so good as in case of 10 Å/sec deposition rates i.e. variation in grain sizes is more. But in case of deposition rate of 5 Å/sec as shown in figure 5(a),5(b), the grains are poorly distributed over the Si surface and grain sizes are coarse & uneven in size. The grains are in the sizes of 21-28 nm which can be improved by annealing.

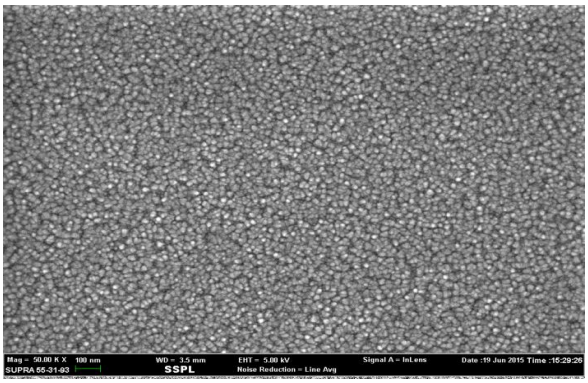

Fig: 6(a). SEM micrographs of CdTe at 50KX magnification with 5KV at deposition rate of 5 Å/sec

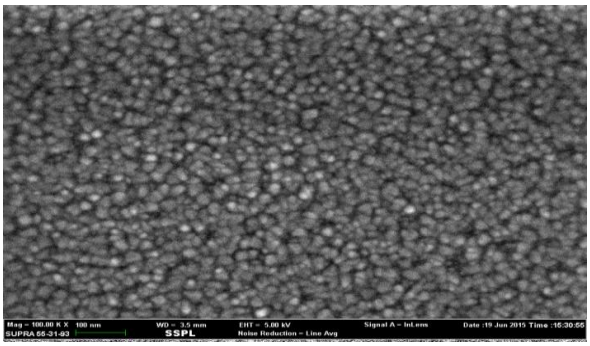

Fig: 6(b). SEM micrographs of CdTe at 100KX magnification with 5KV at deposition rate of 5 Å/sec

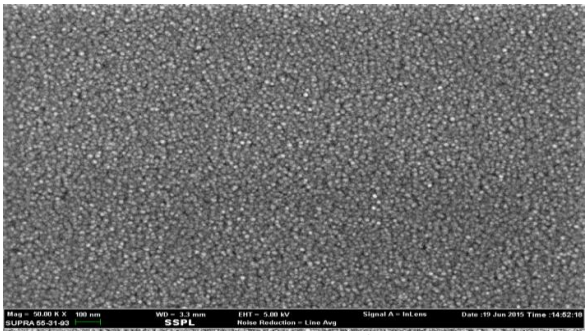

Fig: 7(a). SEM micrographs of CdTe at 50KX magnification with 5KV at deposition rate of 10 Å/sec

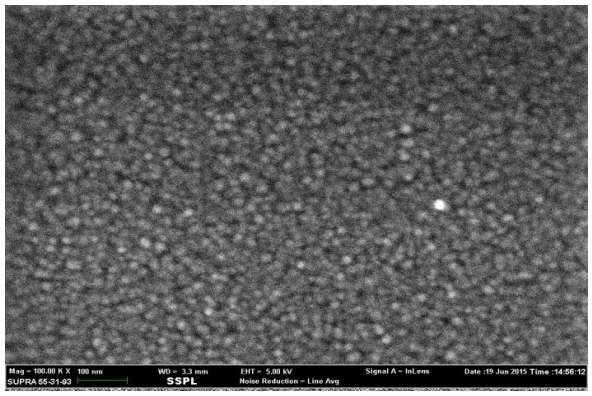

Fig: 7(b). SEM micrographs of CdTe at 100KX magnification with 5KV at deposition rate of 10 Å/sec

5. Conclusion

Thin films of CdTe are prepared by thermal evaporation process on silicon substrates by 1, 5 & 10Å/sec deposition rates. Deposited films thicknesses are measured at different points on Si substrate by dektek surface profiler and compared with the film thickness value shown by Digital Thickness Monitor (DTM) using piezoelectric quartz transducer of having and this variation is found to vary 5-10%. Actually, a comparison is done between film deposited on Si substrate and quartz which are placed close together in the vacuum chamber. This variation can be minimized by reducing the gap between them & regular cleaning of quartz. Also by doing a set of repetitive experiments we can reduce this variation. XRD analysis shows that the CdTe films are polycrystalline with preferential orientation of (111) plane with cubic phase for all the deposition rates of 1, 5 & 10Å/sec.SEM micrographs at 50KX & 100KX magnification shows that film obtained for CdTe at 10 Angstrom/sec is smoother, void free, uniform and regular granular shaped grains than the 5 & 1Å/sec deposition rate. Though comparatively at 1Å/sec deposition rate, microstructure of CdTe is better than 5Å/sec deposition rate. The grain sizes of CdTe at 1, 5 & 10Å/sec is estimated to be in the range of 19-25, 21-28 & 17-20 nm respectively. The EDX analysis shows that the Te/Cd ratio at 1, 5 & 10Å/secis 0.98, 1.14 and 1.18 respectively. Thus we can say CdTe deposition rate of 1 Å/sec is more favorable because of high intensity peaks for preferential (111) plane indicating good crystalline cubic structure, good grain size along with better uniformity on Si substrate and very close to stoichiometric ratio (Te/Cd =1).

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