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EFFECT OF ANNEALING ON THE OPTICAL PROPERTY OF RF-SPUTTERED CdTe THIN FILM

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ABSTRACT

The optical property of CdTe thin film is important for applications such as the compound semiconductor type solar cells. CdTe films are prepared by RF sputtering at various substrate temperature between 25℃ and 300℃, then, annealed in argon gas environment at 400℃. The annealing process of the thin film caused variation in the film structure and the composition of films. The deformation of CdTe thin film was observed by X-ray diffractometry. After annealing, the grain size increased and the portion of the non-crystalline CdTe reduced. Futhermore, the structure of sputtered CdTe film grown at the substrate temperature more than 250℃ was enhanced in the (111) direction of zincblend structure. There was a discrepancy, in the spectroscopic ellipsometer spectrum, between the single crystal CdTe and the sputtered CdTe thin films, especially in the region over 3.2eV. An oxidation layer was found on the CdTe thin film by spectroscopic ellipsometry analysis.

INTRODUCTION

As single crystal CdTe is used for the infrarad detector, polycrystalline CdTe thin films have been employed for the fabrication of the compound semiconductor type solar cells. Generally polycrystalline CdTe film is deposited as light absorption layer on glass substrate with transparant electrode layer such as SnO_2 or ITO.[1] Therefore understading of the optical property of CdTe thin film is important for applications. CdTe films have been prepared by various methods such as chemical electro deposition[2], thermal evaporation[3], e-beam evaporation[4] etc.. Thermal evaporated CdTe films showed problems in annealing, because the film evaporates altering the chemical composition of the film. E-beam evaporated film also appeared the decomposition of evaporant material. RF sputtering of CdTe presents the merit because the deposited film shows the similar composition of the source material[5] comparing with the evaporated films. In this paper, the optical property of RF sputtered CdTe films is investigated.

EXPERIMENT

CdTe was RF sputtered on a c-Si substrate with SiO_2 layer. The SiO_2 was deposited intentionally for the easy analysis of ellisometry as well as for diffusion barrier of CdTe into c-Si. The thickness of the deposited SiO_2 was 1143 Å. Sputter chamber is pumped to base pressure 10^{-6} Torr, then filled with argon gas to working pressure 10^{-3} Torr. Substrate is located 5 cm above the target. Keeping RF power at 40 W, the films were grown up to about 3000 Å at deposition rate of 100 Å. The CdTe films were prepared at various substrate temperature between 25℃ and 300 ℃. The film samples were followed by annealing in argon gas environment at 400℃ during 30 minutes. The thickness of the films were measured by α-step before and after annealing. The effects of annealing on CdTe thin film was studied by X-ray diffractometry and also by spectroscopic ellipsometry.

RESULTS AND DISCUSSION

The variation of the thickness through the annealing of RF sputtered CdTe film is summarized in Table 1. The heat treatment during annealing provokes evaporation of film material resulting reduction of film thickness.

Table 1. The variation of CdTe film thickness by annealing.

substrate tempera-ture	film thick ness of before annealing (Å)	film thick ness of after annealing (Å)	difference
25℃	3571	—	—
150℃	3298	3101	-197
200℃	3918	3813	-105
250℃	3700	3676	-24
300℃	3667	3728	+51

The thickness difference before and after annealing depends on the substrate temperature at which the film was grown. Film grown on the substrate at room temperature was distingushed by the film surface after annealing so rough that the measurement by α-step failed.

The RF sputtered CdTe specimen was invesigated by XRD to see the film structure. In Fig. 1, the principal peaks around 23.7° show that the CdTe film has grown (111) direction.[8] CdTe films show also the peak for (220) (311) around 38° and 46° respectively.[9]

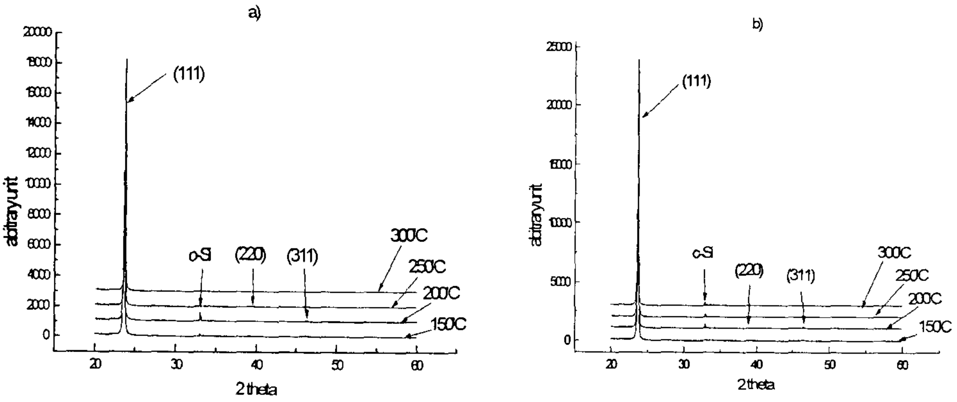

Fig 1. X-ray diffraction spectrum of RF sputtered CdTe films.
(a) before annealing (b) after annealing

In Fig. 1, the principal (111) peak appears in all films prepared at different substrate temperature, while (220) and (311) peaks vary according to the samples.

Fig. 2(a) and (b) show the shift of principal peaks through annealing. A quantitative list of the shifts is summarized in Table 2. During the growth, the substrate temperature is an important parameter for the film structure of CdTe film as shown in Fig. 2(a).

The principal peaks were shifted toward 23.72° all together through the annealing, even though the samples were prepared at different temperatures. This effect can be explained by the recrystallization of the CdTe film during the heat treatment[9]. In Table 2, the full width half maximun (FWHM) values reduced after annealing. It means the grain has grown up during annealing.

The shift of peaks are not the same for the samples grown at different substrate temperature. The shift for the film grown at higher substrate temperatute is smaller, reflecting the larger grain size and the better crystallinity in (111) orientation. Comparing the samples of the substrate temperature of 250℃ and 300℃, both have the same shift. However, the peak for the film grown at 300℃ is

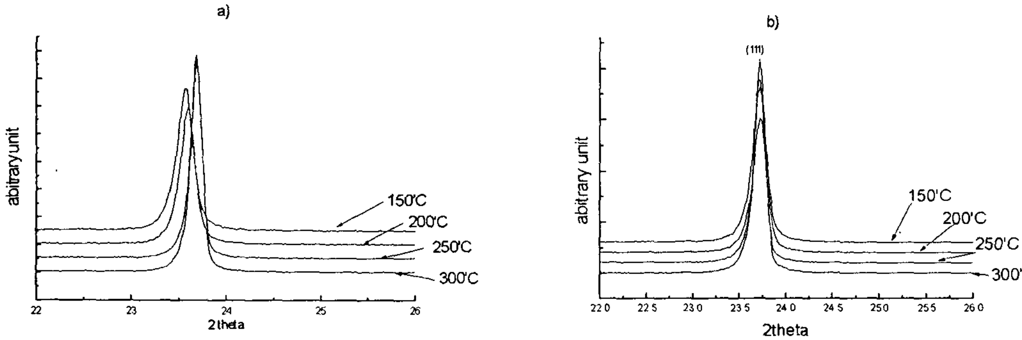

Fig 2. (111) peak shift by annealing.
a) before annealing, b) after annealing.

Table 2. (111) positions in XRD spectrum.
Here, I/Io is the ratio of (111) peak to c-Si peak.

temperature		2 theta of (111) plan	distance of (111) plan (Å)	I/Io	FWHM	2 theta of (220),(311)plans
150℃	before annealing	23.56°	3.773	45	0.184	38.96°, 46°
	after annealing	23.72°	3.748	75	0.149	39.28°, 46.46°
200℃	before annealing	23.58°	3.770	51	0.172	46.1°
	after annealing	23.72°	3.748	62	0.171	46.48°
250℃	before annealing	23.68°	3.754	66	0.122	39.28°, 46.34°
	after annealing	23.72°	3.748	84	0.121	46.44°, 48.56°
300℃	before annealing	23.68°	3.754	69	0.121	46.32°
	after annealing	23.72°	3.748	97	0.119	46.5°

higher, which corresponds larger grain size. The grain size of films, prepared at the substrate temperature more than 250℃, differs negligiblly.

In Table 3, the size of grain of different orientations are compared. The films prepared at a higher substrate temperature shows the smaller ratio of I(hkl)/I(111), which means that the grain of direction (hkl) reduceed. In other words, the film shows the tendency to grow in the selected (111) orientation.

The effect of annealing to the film structure was found not the same, according to the substrate temperature under which the films have been grown. The films, grown under the substrate temperature below 250 ℃, transforms into a structure of increasing I(hkl)/I(111) ratio. It means that the grain of orientation other than (111) grows larger.

In the mean while, the films of the substrate temperature above 250℃ shows reduction of I(hkl)/I(111) ratio through the annealing, which means the film structure changed into the (111) orientation.

The optical characteristics of the CdTe film samples were investigated by the spectroscopic ellipsometry. For the ellipsometric analysis, the films were assumed to have the structure shown in Fig. 3. The CdTe films have the thickness of around 3500Å. The probing light

Table 3. Comparative size of XRD peaks

temperature		I(111)	I(220)/I(111) ($\times 10^{-3}$)	I(311)/I(111) ($\times 10^{-3}$)	I(311)/I(220)
150℃	before annealing	1	3.12	4.38	1.403
	after annealing	1	2.39	6.79	2.841
200℃	before annealing	1	0	4.43	–
	after annealing	1	0	8.42	–
250℃	before annealing	1	2.62	2.28	0.870
	after annealing	1	0	1.39	–
300℃	before annealing	1	0	2.06	–
	after annealing	1	0	0.85	–

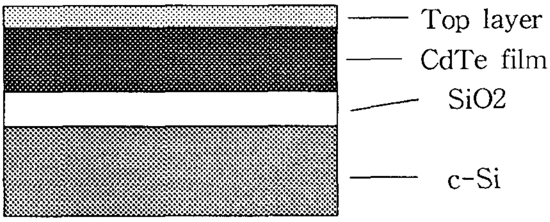

Fig 3. Model of the CdTe film. Bulklike CdTe film is deposited on c-Si substrate with SiO_2 layer. Surface has roughness and void.

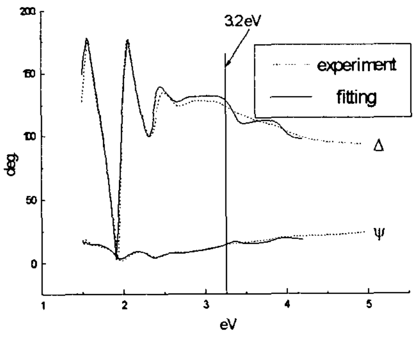

Fig 4. Spectroscopic ellipsometer spectrum.

of wave length should have enough the penetration depth to touch the substrate and film interface.

The penetration depth vs. photon energy curve in Fig. 5, decreases abruptly around 3.2 eV, while below 3.2 eV it keeps the value over 1400Å. Therefore, in above 3.2 eV region, spectrscopic ellipsometer measurement would give the information of only the upper part of the CdTe film. For this reason, the ellipsometry analysis was treated in the region of 1.5~3.2 eV, where 1.5 eV is the lower limit of measurement of the apparatus.

Fig 6. is the complex dielectric function of single crystal CdTe. The imaginary part of the dielectric function of c-CdTe has peaks at 3.4 eV and 3.8 eV. ε_1 curve also shows discontinuity at 3.45 eV and 4.0 eV. These peaks, typically found in semiconductor crytalline matrieals because of the direct band gap, disappear giving smooth curve in the polycrystalline material such as the RF sputtered films. This aspect provides another reason to discard the values above 3.2 eV in the analysis of the RF sputtered CdTe films. The result of SE analysis are summarized in Table 4 .

The films showed the porous toplayer without exception. This would be the consequence of surface roughness because of the damage of surface layer during the annealing. The model with CdTeO as an upper surface layer provides better fitting as in Fig 7. This leads to assume the presence of oxide surface layer.

The ellipsometry analysis also provides the thickness variation of films during the annealing. The thickness changes depending on the substrate temperature during the film formation. The films of lower substrate temperature make greater loss. The film grown at the room temperature showed too rough surface to analyze the meaningful thickness. The analysis revealed the tendency of the smaller loss of thickness during annealing in the film prepared at higher substrate temperature. It reflects that the loss of film by the evaporation of CdTe during the annealing decreases rapidly with the enhancement of (111) film orientation.

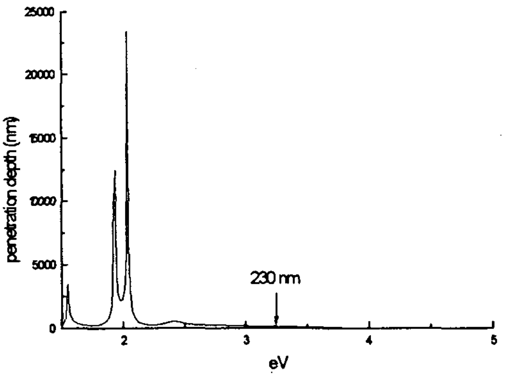

Fig 5. Penetration depth calculated by dispersion relation of nonconducting medium.

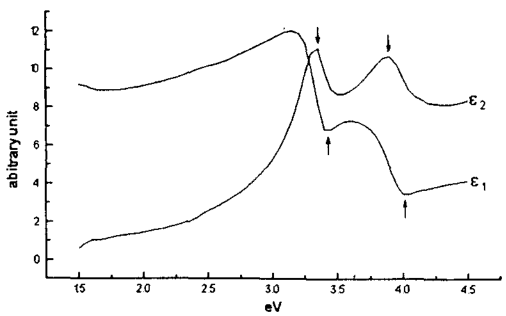

Fig 6. Complex dielectric function of single crystal CdTe[10] " ↑ " indicates singularities.

Table 4. Film structure obtained from ellipsometry anaysis.
σ is standard deviation of fitting.

substrate temperature	before anneal (Å)	annealed (Å)	
150℃	(131/3452/sub) $\sigma = 0.263$	(208/3316/sub) $\sigma = 0.279$	film structure; void+CdTeO+CdTe/ bluk CdTe/sub
200℃	(116/3375/sub) $\sigma = 0.292$	(172/3337/sub) $\sigma = 0.316$	
250℃	(102/3341/sub) $\sigma = 0.301$	(199/3293/sub) $\sigma = 0.303$	
300℃	(66/3479/sub) $\sigma = 0.307$	(132/3396/sub) $\sigma = 0.281$	

substrate temperature	before anneal (Å)	annealed (Å)	
150℃	(131/3451/sub) $\sigma = 0.264$	(197/3326/sub) $\sigma = 0.289$	film structure; void + CdTe / bluk CdTe / sub
200℃	(107/3441/sub) $\sigma = 0.326$	(162/3421/sub) $\sigma = 0.372$	
250℃	(91/3524/sub) $\sigma = 0.380$	(192/3409/sub) $\sigma = 0.389$	
300℃	(79/3458/sub) $\sigma = 0.307$	(123/3400/sub) $\sigma = 0.282$	

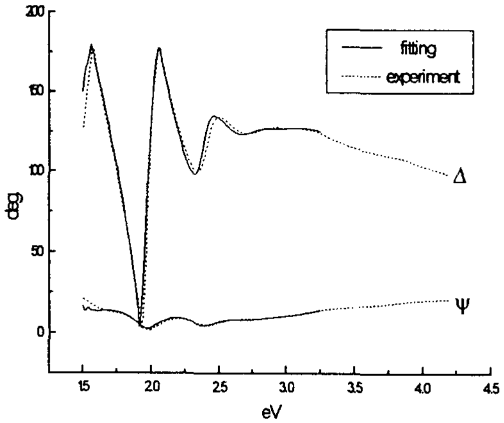

Fig 7. Improved spectroscopic ellipsometer fitting.

CONCLUSION

The RF sputtered CdTe films grown on Si substrate at various temperatures were investigated by XRD. The XRD spectrum of the films showed the (111) principal peack without exception. The annealing improved the crystallivity in the (111) orientation for the films prepared at the substrate temperature above 250℃, while the improvement was not found in the films prepared at the lower temperature.

The RF sputtered CdTe film was also studied by the spectroscopic ellipsometer to measure the variation of the thickness of films. The reduction of the film thickness was found. The difference in thickness before and after annealing varies according to the substrate temperature during the film growth. The film grown at the substrate temperature 250℃ did not vary in thickness during the annealing, however, the film prepared at 150 ℃ reduced to a half.

Being grown on the substrate 250℃ then annealing at 400℃, the RF sputtered CdTe film of bulk phase structure could be obtained. From the spectroscopic ellipsometer analysis, an oxide layer on the CdTe film surface was found.

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