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Annual Subcontract Report
1 June 1987 - 31 May 1988

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Georgia Institute of Technology
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Prepared under Subcontract No. XL-7-06031-1

SERI

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

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1. INTRODUCTION

Thin-film CdTe solar cell is a promising photovoltaic technology with the potential of eventually producing terrestial electric power competitively with conventional sources. CdTe has nearly the optimum bandgap, 1.5 eV, for photovoltaic solar energy conversion. Single junction thin film heterojunction solar cells, such as CdTe/CdS/ITO/glass (substrate), with AM1 efficiencies higher than 10% have been reported,[1] and optimization of the properties of CdTe and window films may increase the conversion efficiency to the 15% range. Any further improvements are unlikely due to interface recombination, the inefficient use of the solar spectrum, and other losses.[2] However, the conversion efficiency can be significantly increased if two solar cells of direct gap semiconductors with appropriate bandgaps are used in tandem.[3] The optimum bandgaps for the upper and lower cells are 1.65 - 1.75 eV and 1.0 - 1.1 eV, respectively. The use of a thin CdTe solar cell as the upper cell reduces the efficiency of the lower cell because its bandgap is smaller than the optimum energy. Therefore, the main objective of this program is to develop a solid solution of CdTe, MnTe and ZnTe ($E_g = 2.25$ eV) films with a bandgap of 1.65 - 1.75 eV to be used as the absorber material for the upper member of the tandem cell. We propose to investigate three promising alloys, namely $Cd_{1-X}Zn_XTe$ and $Hg_{1-X}Zn_XTe$ by MBE growth and $Cd_{1-X}Mn_XTe$ by MOCVD techniques.

In the first year of program, we concentrated on growing CdTe and CdZnTe by MBE and CdTe and CdMnTe by MOCVD. [The CdS/SnO_2/glass substrates were provided by Ametek Applied Materials Laboratory, Pennsylvania.] All the as-grown films were characterized by several techniques like X-ray diffraction (XRD), Surface Photovoltage Spectroscopy (SPV), Infrared Spectroscopy (IR), Raman and Photoluminescence, and Auger Electron Spectroscopy (AES) for composition, bulk uniformity, thickness, film and interface quality. There are a few reports on MOCVD grown CdMnTe and MBE grown CdZnTe single crystal films but there are no reports on growing polycrystalline CdMnTe and CdZnTe by MOCVD or MBE techniques.

Hence, we have grown single crystal films simultaneously to understand the growth conditions of polycrystalline films. Front-wall type solar cells were fabricated in collaboration with Ametek (AML) using CdTe, CdZnTe, and CdMnTe polycrystalline films as absorber. In this annual report we present our results on characterization and device fabrication and measurements of CdTe, CdZnTe, and CdMnTe films.

2. TECHNICAL PROGRESS

2.1 Growth of CdZnTe and CdMnTe Films by MBE and MOCVD

2.11 CdZnTe by MBE

First, fifteen MBE growth runs were made with widely varying conditions in order to identify as quickly as possible the important parameters for the growth of good solar cell materials. Multiple substrates of glass, glass/SnO_2, and glass/SnO_2/CdS were used in each run. In all, forty-five layers were produced and a listing of all runs with growth conditions and some of the measured properties is given in Table 1. The interaction of substrate type, growth temperature, ZnTe/CdTe flux ratio, Sb doping, and laser assisted doping was investigated.

Undoped layers with constant ZnTe/CdTe flux ratio were grown with substrate temperatures between 100 and 300°C. Auger measurements on one sample grown at 250°C confirmed the predicted alloy ratio ($Zn_{.25}Cd_{.75}Te$) within experimental error. Auger measurements have not been made on layers grown at other temperatures and may not be necessary since the evaluations of the material thus far indicate the 250°C is the optimum growth temperature.

We also grew CdZnTe films with elemental source materials (Cd, Zn, Te) instead of using compound materials (ZnTe, CdTe), to increase film purity. Table 2 shows the growth parameters used here. To insure high quality material, a substrate temperature of 300°C is necessary. However, the evaporants did not stick well initially at this temperature so that the substrate temperature was started at 250°C before being increased to 300°C. In later runs, as seen in Table 2, high quality films were obtained at 275°C with the advantage that the temperature could be held constant throughout the run, eliminating any possible variation in composition due to this variable.

TABLE 1. LISTING OF LAYERS GROWN WITH GROWTH PARAMETERS

Sample	Substrate	Deposition Zn(x)Cd(1-x)Te	Substrate Temp °C	Deposition Time (hrs.)	Flux (10˚ - 7torr)				Thickness (µm)	Zn-Cd Ratio	Method	Band Edge (nm)	Bandgap (eV)
					Before CdTe	Before ZnTe	After CdTe	After ZnTe					
E87-1	glass	0.29	280	3			7.4	3.3	2.20	.25/.75	Auger	768	1.63
	glass+SnO								2.30				
	glass+SnO+CdS								2.20				
E87-2	glass	0.29	200	3			2.6	8.6	2.20			790	1.68
	glass+SnO								2.29				
	glass+SnO+CdS												
E87-3	glass	0.29	200	4			8.6	2.9	3.90			790	1.68
	glass+SnO	(+ZnTe cap)							3.00				
	glass+SnO+CdS												
E87-4	glass	0.25	150	3			10	3.3	3.30			790	1.68
	glass+SnO								2.70				
	glass+SnO+CdS								2.98				
E87-5	glass	0.25	100	3			8.4	2.7	2.40			790	1.68
	glass+SnO								2.40				
	glass+SnO+CdS												
E87-6	glass	0.25	229	3			9.7	3.3	2.40			790	1.68
	glass+SnO								2.60				
	glass+SnO+CdS								3.40				
E87-7	glass	0.25	250	3			9.3	2.9				748	1.66
	glass+SnO		then									799	1.64
	glass+SnO+CdS		300										
E87-8	glass	0.25	200	3			9.2	4					
	glass+SnO+CdS						9.2	3.4					
E87-9	glass	0.30	200	3			7.7	4.6					
	glass+SnO+CdS						7.8	9					
E87-10	glass	0.9	200	3			8.9	6					
	glass+SnO+CdS						6.4	6.8					

TABLE 1. LISTING OF LAYERS GROWN WITH GROWTH PARAMETERS (Continued)

Sample	Substrate	Deposition Zn(x)Cd(1-x)Te	Substrate Temp °C	Deposition Time hrs.	Flux (10ˆ - 7torr) Before CdTe	ZnTe	After CdTe	ZnTe	Thickness (µm)	Zn-Cd Ratio	Method	Band Edge (nm)	Bandgap (eV)
E87-11	glass glass+SnO+CdS	0.69	200	3	11	2.1	9	9				760	1.63
E87-12	glass glass+SnO+CdS	0.89	200 + laser	3	11	3 0.006	9.1	1.9 0.006				768	1.62
E87-13	glass glass+SnO+CdS	0.25	200 + laser	3	9.5	4 0.006	8.4	3 0.006				719	1.73
E87-14	glass glass+SnO+CdS	0.39	200 + laser	3	9	5 0.006	7.3	4.2				712	1.74
E87-15	glass glass+SnO+CdS	0.5	200 +laser	3	7	7	6	12					

TABLE 2. GROWTH CONDITIONS AND FILM THICKNESSES AND BANDGAPS FOR CdMnTe GROWN ON CdS/Sn0_2/glass SUBSTRATES

ID	Target Composition	T_{SUB} (°C)	Dep. Time (hrs.)	Beam Flux (x 10^{-7} torr) (Zn/Cd,Sb)	Film Thickness (μm)	E_G(SPV) (eV)
R87-46	CdTe	250	1.0	0, .022	?	1.51
		300	2.0			
R87-44	$Cd_{.75}Zn_{.25}Te$	250	1.0	0.165, 0	?	1.56
		300	3.0			
R87-47	$Cd_{.75}Zn_{.25}Te$	250	1.0	0.29, 0.007	0.5	1.03
		300	2.0			
R87-50	$Cd_{.75}Zn_{.25}Te$	250	0.25	0.263, 0.014	1.0	1.68
		275	2.75			
R87-51	$Cd_{.75}Zn_{.25}Te$	275	3.0	0.286, 0.056	1.1	1.69
R88-2	$Cd_{.75}Zn_{.25}Te$	275	3.0	0.367, 0.005	1.1	1.70

2.12 CdMnTe by MOCVD

We made attempts to grow CdMnTe films by MOCVD on single GaAs (111) substrate, with and without CdTe buffer layer. Process conditions for the first 9 runs are listed in Table 3. Growth temperature for CdMnTe films was in the range of 400-450°C, reactor pressure was 250 torr, Te partial pressure was fixed at 127 mtorr, Mn partial pressure was 3-4 mtorr, and Cd partial pressure was varied in the range of 4.6-18.5 mtorr to control the bandgap, composition, and surface morphology. CdMnTe films were obtained with thickness in the range of 0.5 to 1.5 um.

2.13 Doped CdZnTe by MBE

It is known from literature that CdTe films can be doped with Sb using photoassisted MBE technique.[4] In our laboratory the same method was used to dope CdTe and CdZnTe with Sb. In order to dope Sb Ar^+ laser (488 nm) line with 800 mW power was used during growth. The incorporation of Sb in CdZnTe films was verified from in-situ Auger measurements as shown in Figure 1. Also, we grew ZnTe film on top of CdTe and CdZnTe polycrystalline film in order to fabricate p-i-n solar cells. Using the same method the ZnTe film was also doped with Sb (Figure 2).

2.2 Characterization of CdZnTe and CdMnTe Films

2.21 X-Ray Diffraction

X-ray diffraction measurements were done using Phillips X-ray diffractometer. XRD measurements were performed to estimate the composition, and to identify the other phases of CdZnTe. Figure 3 shows the XRD of one of the polycrystalline (CdZnTe:Sb/CdS/Sno_2/glass) samples. The peaks at 23.7900, 39.5000, and 46.7100 correspond to CdZnTe, and all other peaks are due to CdS/SnO_2/glass substrate. The lattice constant of the film was calculated using the equation $a = d\sqrt{h^2 + k^2 + l^2}$, where "a" is the lattice constant, h, k, l are the indices. In order to determine the lattice constant more accurately we used an extrapolation

TABLE 3. GROWTH CONDITIONS OF PRELIMINARY CdMnTe RUNS ON GaAs BY MOCVD

			CdTe Growth				CdMnTe Growth						
Sample Name	Material Grown	Reactor Pressure (torr)	T_s °C	Time (min)	P_{Tc} (mtorr)	P_{Cd} (mtorr)	T_s °C	Time (min)	P_{Te}	P_{Cd}	P_{Mn}	CdTe Thickness (um)	CdMnTe Thickness (um)
A0402871	CdMnTe	250					450	120	127	9.3	3.3		0.5
A0403871	CdMnTe	250					420	120	127	16.5	3.3		1.5
A0403872	CdMnTe	290					320	120	127	16.5	3.3		3.0
A0406671	CdMnTe	290					400	120	127	16.5	3.3		2.0
A0407871	CdMnTe	280					400	120	127	9.3	3.3		1.6
A9413876	CdTe/ CdMnTe	200	390	90	136	20	420	90	127	9.3	3.3		3.0
A0414671	CdTe/ CdMnTe	260	360	90	136	20	420	90	127	4.6	3.3		3.9
A0419671	CdTe/ CdMnTe	290	360	90	136	29	420	90	127	9.3	3.3		3.5
A0425671	CdTe/ CdMnTe	290	360	90	136	20	420	90	127	4.6	4.0	+2	≈5.6

Substrate to 2" GaAs (111) wafer (LEC grown)

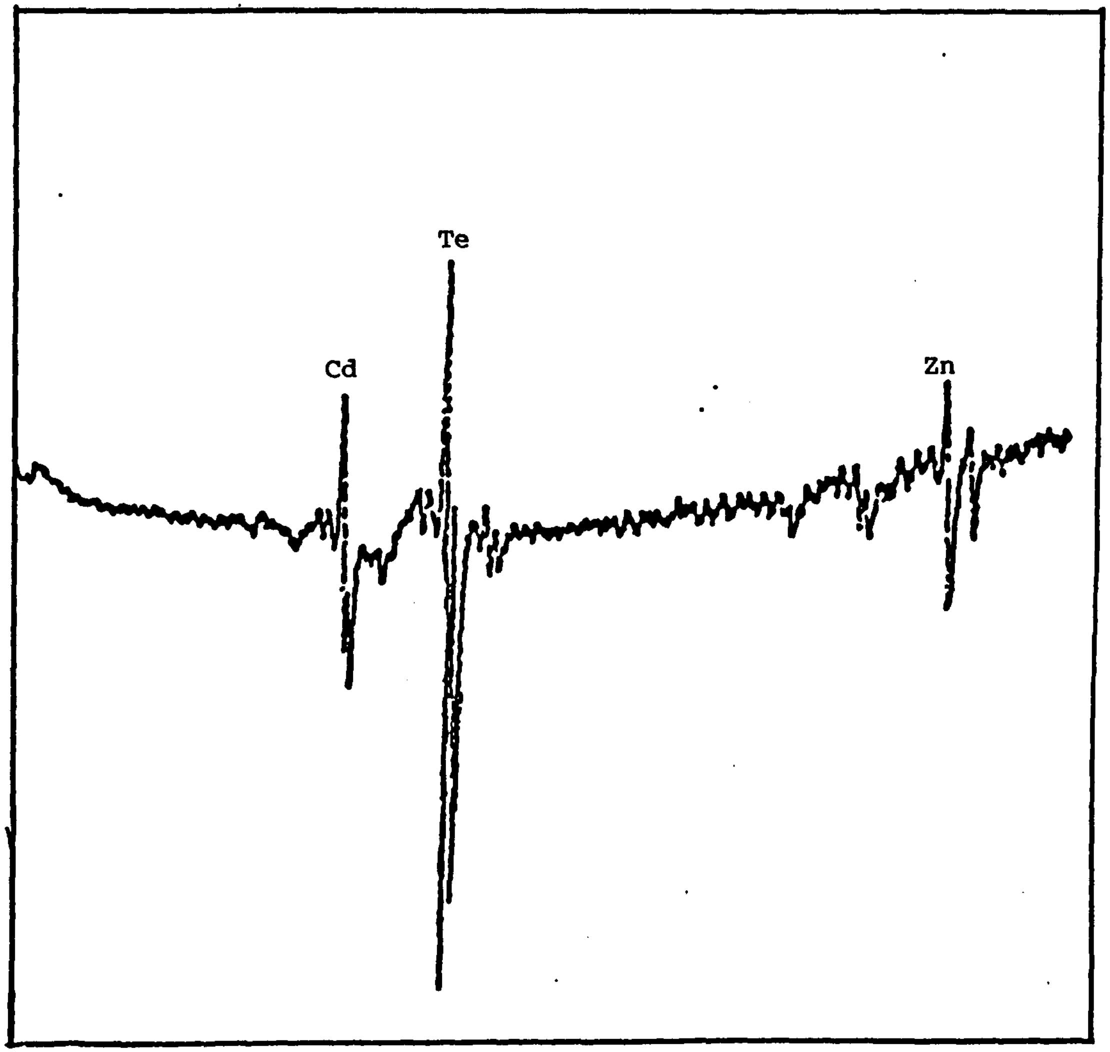

Figure 1. In-situ Auger spectrum of CdZnTe:Sb/CdS/SnO_2/glass.

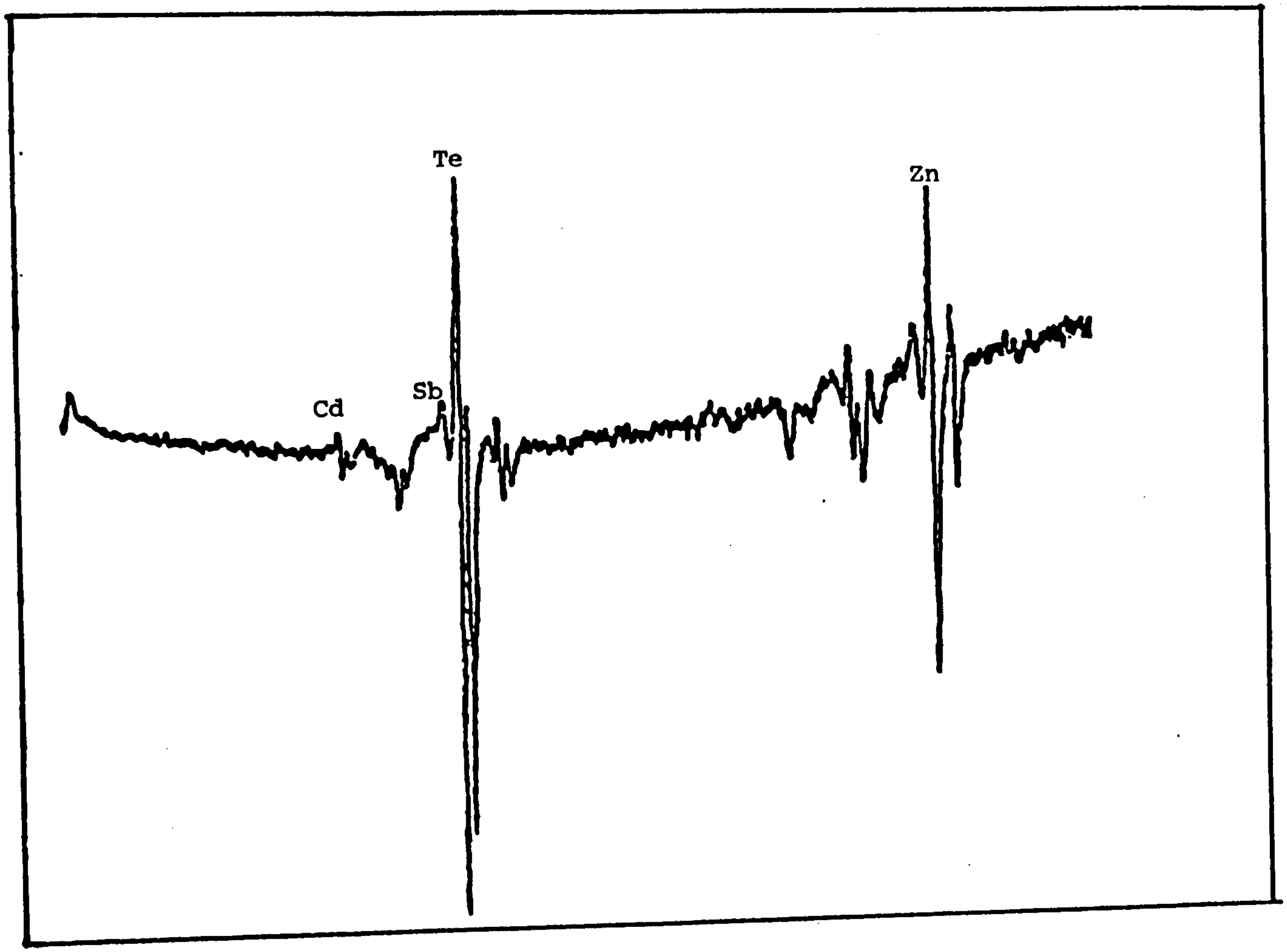

Figure 2. In-situ Auger spectrum of ZnTe:Sb/CdZnTe/CdS/SnO$_2$/glass.

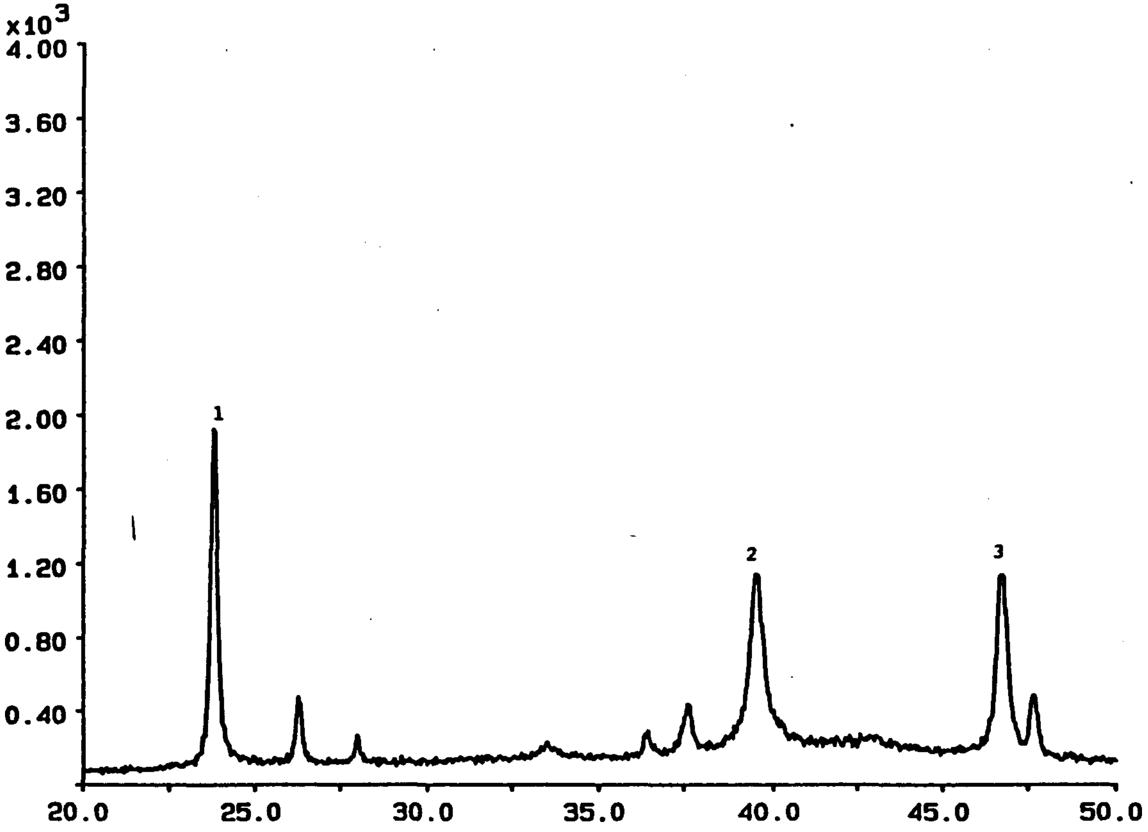

Figure 3. X-ray diffractogram of polycrystalline CdZnTe sample. Peaks marked 1, 2, 3 correspond to CdZnTe and all other peaks arise from substrate.

technique (Nelson-Riley technique).[5] Figure 4 shows the extrapolation plot for CdZnTe sample (R87-46). Knowing the lattice constant, the Zn concentration was estimated from lattice constant versus Zn concentration plot.[6] The estimated Zn value is 40%. Also the XRD indicate that the film has a single phase of CdZnTe since no other lines, other than those due to substrate, are present.

Figure 5 shows the XRD of one of the CdMnTe polycrystalline samples. The peaks at 23.709, 39.394 and 46.528 correspond to CdMnTe films. The other peaks arise from CdS/SnO_2/glass substrate. The lattice constant of the film was calculated as explained above. The Mn concentration was estimated from the equation $a = 6.487 - 0.149 X$, where X is the Mn concentration.[7] The estimated Mn concentration value is 11%.

2.22 Surface Photovoltage Spectroscopy (SPV)

SPV measurements were made on CdTe and CdZnTe films with an electrochemical profiling system. Electrochemical SPV has an advantage over techniques such as optical absorption in that measurements can be made in a depth-resolved fashion so that compositional uniformity and material quality can be determined, by tracking variations in the bandgap and response magnitude, respectively.[8] The SPV measurements were made using an electrolytic solution consisting of 0.2 M NaOH + 0.1 M EDTA (ethylene diammine tetraacteic acid) which forms a Schottky barrier contact on the CdTe or CdZnTe surface. The sample surface is illuminated in the wavelength range 400 nm to 900 nm. Absorbed photons generate electron-hole pairs which drift to and are separated by the surface field and hence induce a surface photovoltage which is subsequently measured there. The experiment is performed under open-circuit conditions to avoid any etching or electroplating at the sample surface.

Figure 6 shows SPV spectra of (a) CdTe, sample E88-7, CdZnTe sample E88-8 and a different CdZnTe:Sb film sample E88-9, grown on CdS/SnO_2/glass substrates by MBE. The SPV cutoff wavelengths indicated the proper bandgaps for CdTe (1.5 eV) and CdZnTe (1.7 eV) while the absorption edges are sharp, particularly for CdTe indicating little sub-bandgap

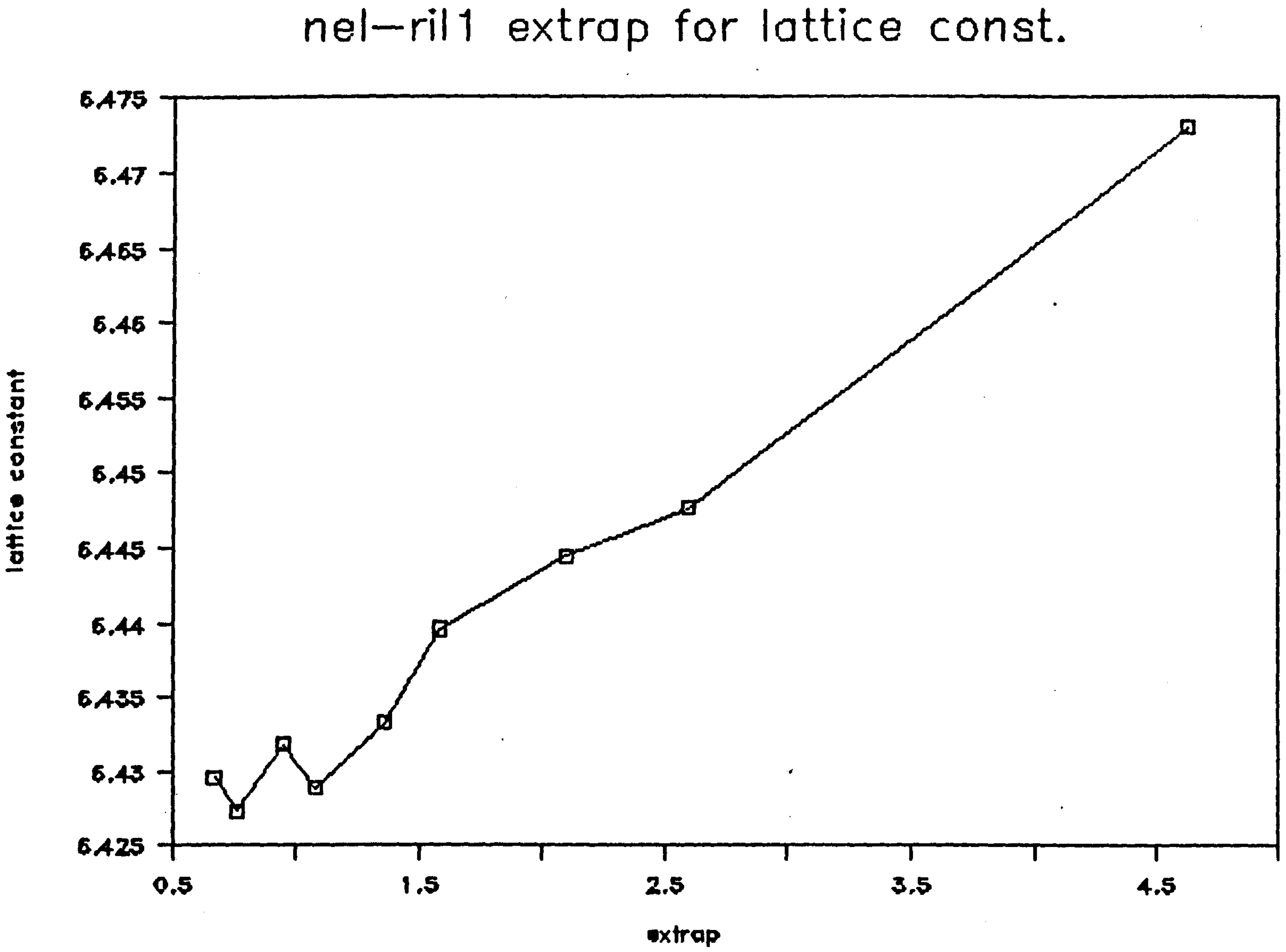

Figure 4. Extrapolation versus lattice constant plot of CdZnTe. The extrapolated lattice constant value is 6.419 A.

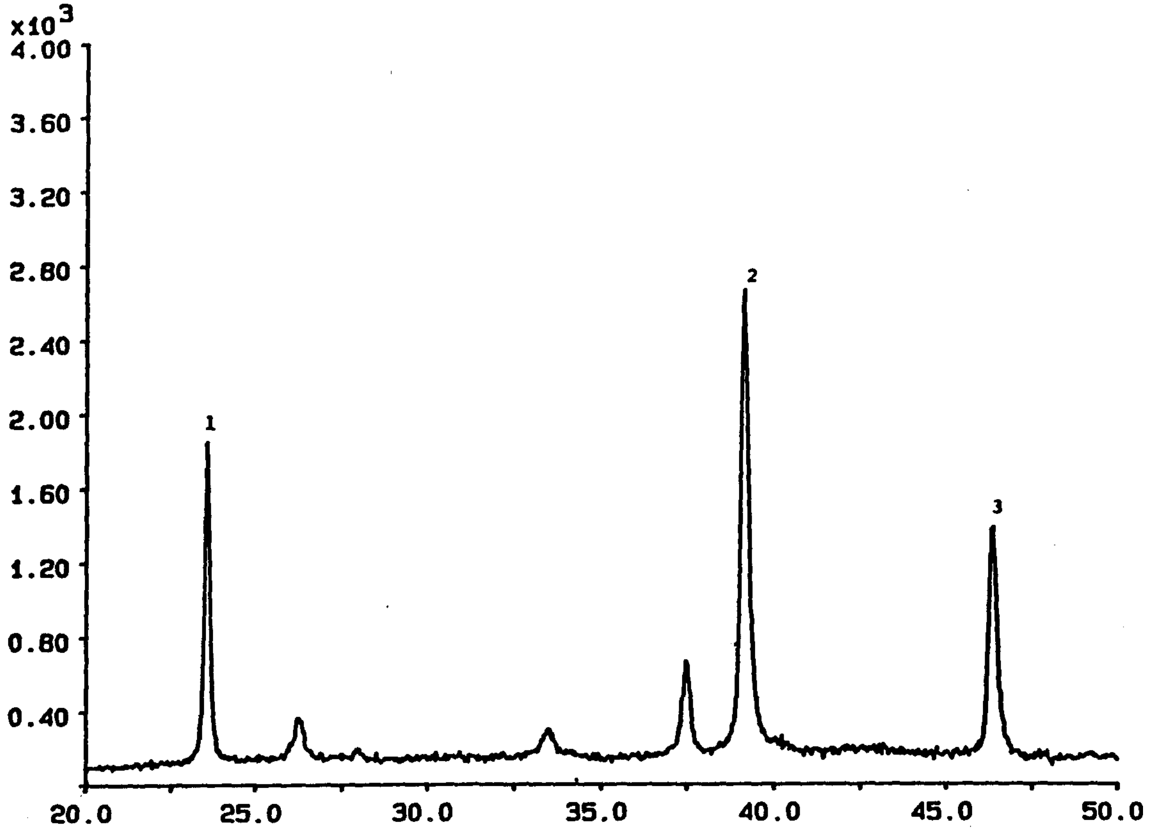

Figure 5. X-ray diffractogram of CdMnTe polycrystalline films. The peaks marked 1, 2, 3 are CdMnTe film and other peaks are due to CdS/SnO$_2$/glass substrate.

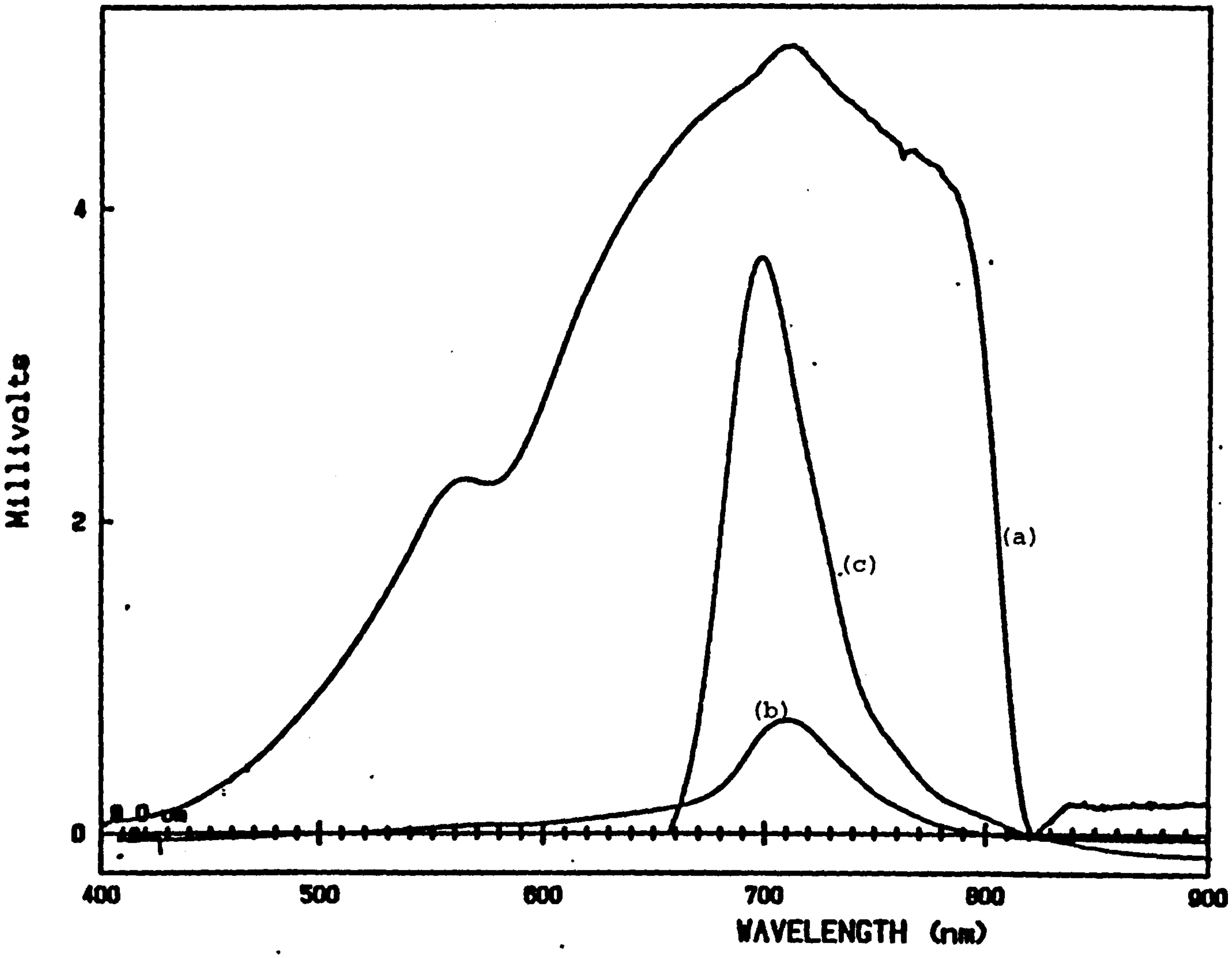

Figure 6. SPV spectra of (a) CeTe, (b) CdZnTe, and (c) CdZnTe:Sb, all of approximately the same thickness.

absorption suggesting high material quality. The relative heights and shapes of these spectra are most likely a result of either change in material quality, i.e. carrier lifetime, or Fermi level position which would change the amount of band bending present at the electrolyte/semiconductor interface.

Figures 7 and 8 show the SPV spectra of CdTe and CdMnTe polycrystalline films grown on CdS/SnO_2/glass substrates by MOCVD. CdTe spectrum has a sharp cut-off edge at 840 nm which corresponds to a bandgap of 1.48 eV, whereas the CdMnTe has a broad absorption edge around 720 nm which corresponds to a bandgap of 1.72 eV. From the bandgap of CdMnTe film, the Mn concentration was calculated using the relation $E_g = 1.50 + 1.34$ eV where X is Mn concentration.[7] The calculated value is 16%.

2.23 Infrared Spectroscopy (IR)

IR spectroscopy is one of the non-destructive characterization techniques for semiconductors. The phonon modes carry information about the quality of films. We have used this technique to characterize CdMnTe thin films of different Mn concentration and thicknesses, grown on GaAs, glass and heavily doped CdS films. IR reflectance measurements on these samples were made from 10-220 cm^{-1}, using a modified Grubb-Parsons interferometer with a Golay cell as a detector. All the spectra were taken with a resolution 2 cm^{-1}.

It is known that CdMnTe alloy has two phonon mode behavior; CdTe-like and MnTe-like modes.[9] In CdMnTe the CdTe-like phonon frequency (140 cm^{-1}) and MnTe-like phonon frequency (180 $cm-^{1}$) do not vary with Mn concentration, but the strengths of modes vary with Mn concentration. The phonon parameters are well known for all Mn concentrations in bulk CdMnTe.

Figure 9 shows the infrared spectra of CdMnTe single crystal films with a CdTe buffer layer for different substrate temperatures. All spectra show two peaks: 140 cm^{-1} corresponds to CdTe-like mode and 185 cm^{-1} corresponds to MnTe-like mode. It is clear from the spectra for substrate temperatures less than 400°C the CdTe-like peak is well pronounced but MnTe-

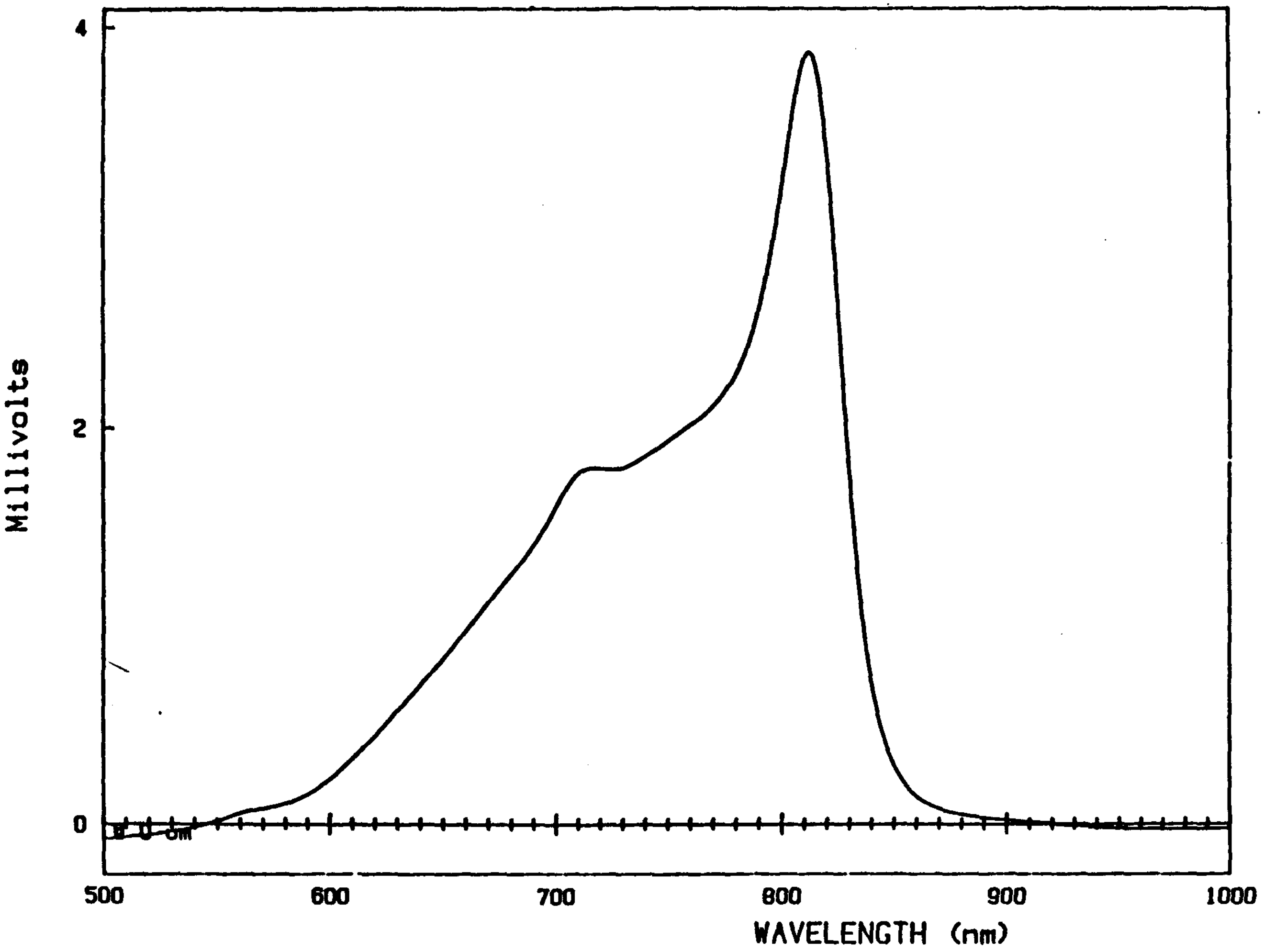

Figure 7. SPV spectrum of MOCVD CdTe polycrystalline film.

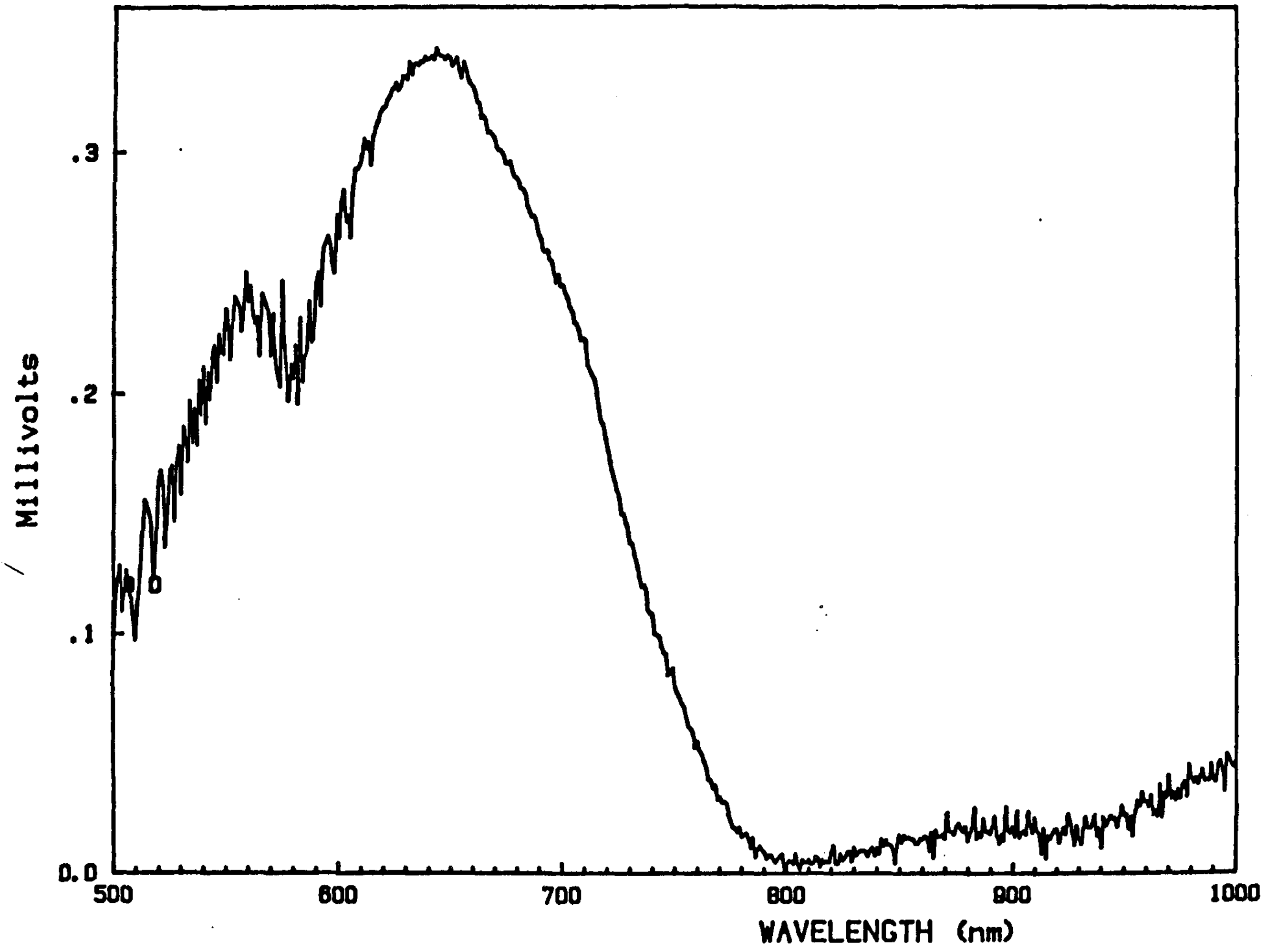

Figure 8. SPV spectrum of CdMnTe polycrystalline film (A-217881).

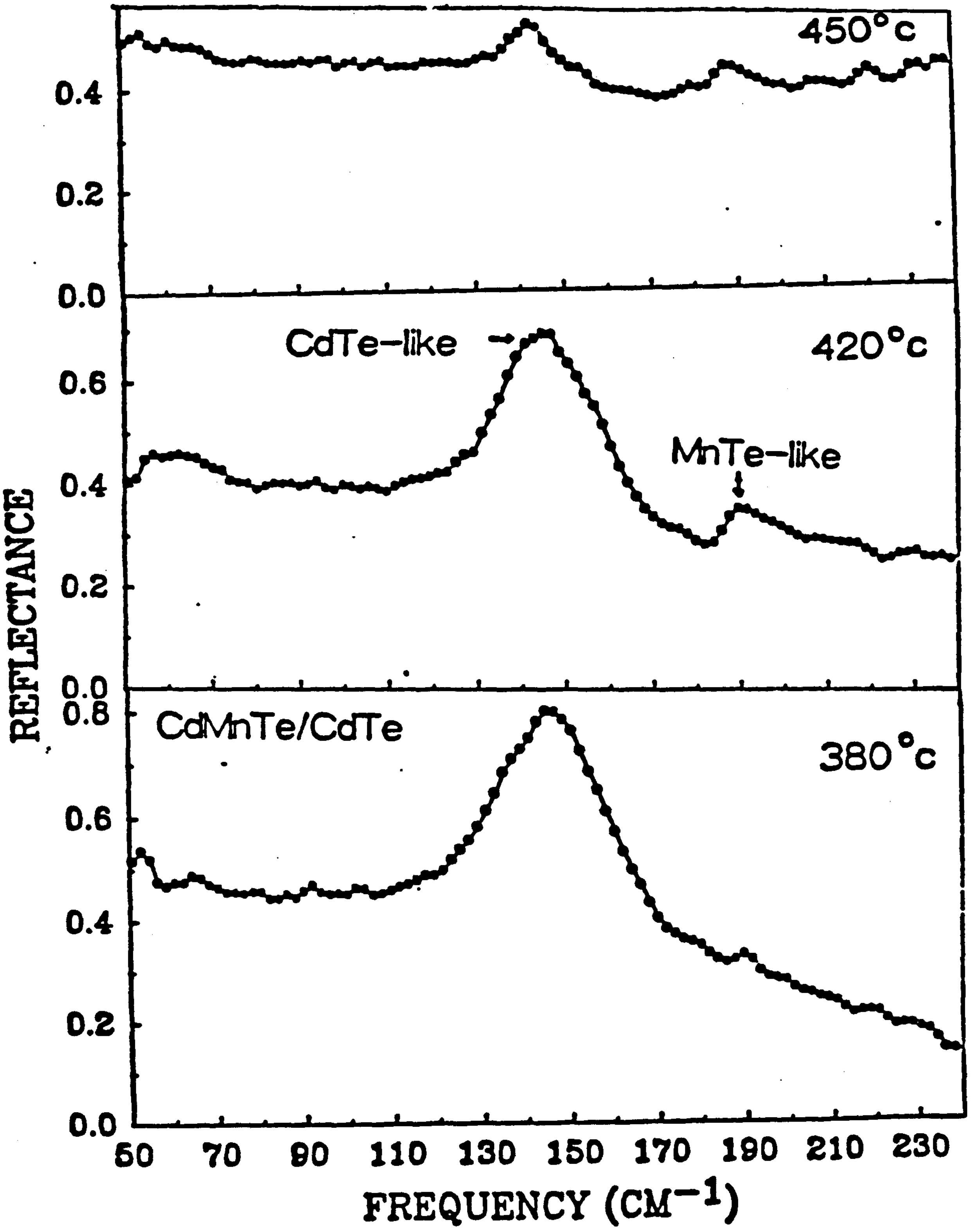

Figure 9. Infrared spectra of single crystal CdMnTe films grown at different substrate temperatures.

like peak appears very weak. This indicates that the Mn concentration is less than 10%. At 420°C substrate temperature the MnTe-like peak is clearly seen, indicating higher Mn concentration (20%). At 450° substrate temperature, even though the MnTe-like mode is stronger, but the CdTe-like mode is weakened. This indicates poor film quality, perhaps more defects. These results suggest that the optimum substrate temperature for good quality single crystal CdMnTe films with greater than 10% Mn is 420°C.

Figure 10 shows the reflectance spectrum of one of the CdMnTe film grown on GaAs substrate. The phonon modes at 140 and 180 cm^{-1} correspond to CdTe-like and MnTe-like modes respectively. In order to estimate Mn concentration in these films, we used a model. According to this model the dielectric function has three terms: lattice, free carrier and interband terms which is given as

$$E(\omega) = E_{\mathrm{lattice}} + E_{\mathrm{free\ carriers}} + E_{\mathrm{interband}}$$

We considered only the lattice term since the reflectivity seems to have no contribution from other terms. Then the dielectric function can be represented by a Lorentzian oscillator for each phonon of the form.

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_{j=1}^{2} S_j \omega^2 / \omega_{\mathrm{To}}^2 - \omega_{\mathrm{To}}^2 - i\Gamma_j \omega$$

where the ω_{TO}, S, Γ and ϵ_{∞} correspond to frequency, strength, damping constant and high frequency dielectric constant respectively. Using the known phonon parameters and standard expressions for reflectivity which include thickness of the films, we fitted the reflectivity data. The theoretical fit is also shown in Figure 10 as a dashed line. From the analysis we find both Mn concentration and thickness of CdMnTe films. Table 4 gives our analyzed values for several samples. We also measured the reflectance of CdMnTe films grown on various substrates under the same conditions. Figures 11-13 show the reflectance of CdMnTe films on

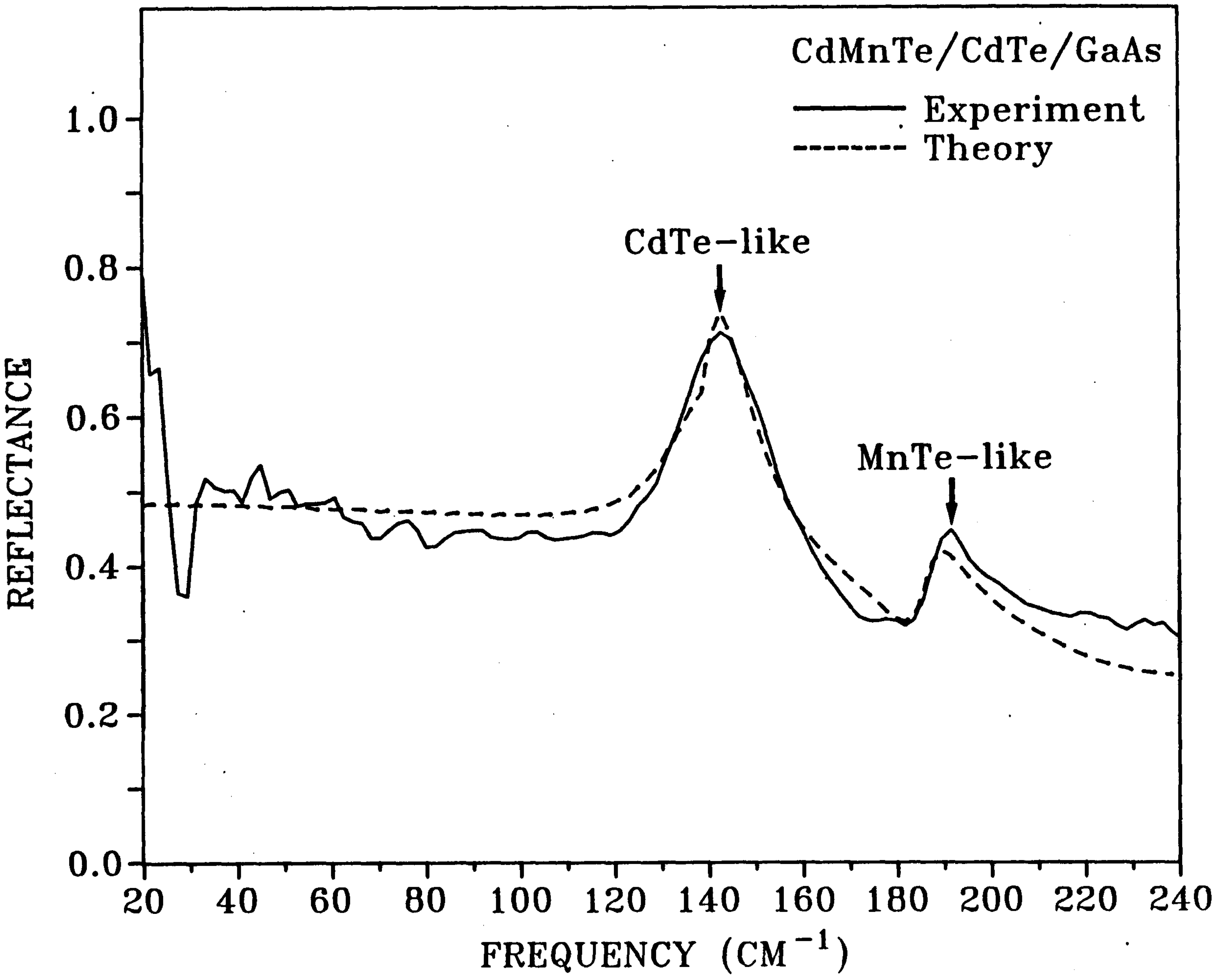

Figure 10. Room temperature measured (solid line) and theoretical fit (dashed line) reflectivity of single crystal CdMnTe (A0504871).

TABLE 4. DERIVED VALUES OF Mn CONCENTRATION AND FILM THICKNESS FROM THE ANALYSIS OF INFRARED SPECTRA OF SINGLE CRYSTAL $Cd_{1-x}Mn_xTe$/CdTe/GaAs (111) FILMS, AND x VALUES FROM PL MEASUREMENTS

	Infrared			PL
	X	Thickness		X
Sample #		CdMnTe μm	CdTe μm	
A0425871	0.25	0.65	1.7	0.28
A0623872*	0.15	1.5	-	0.11
A0918871	0.05	0.78	1.7	0.06
A0925871	0.25	0.70	1.7	0.26**

*In this sample the film was grown on GaAs (111) without CdTe buffer layer.

**PL measurements indicated a variation in the Mn concentration (0.18-0.35). The mean value is quoted.

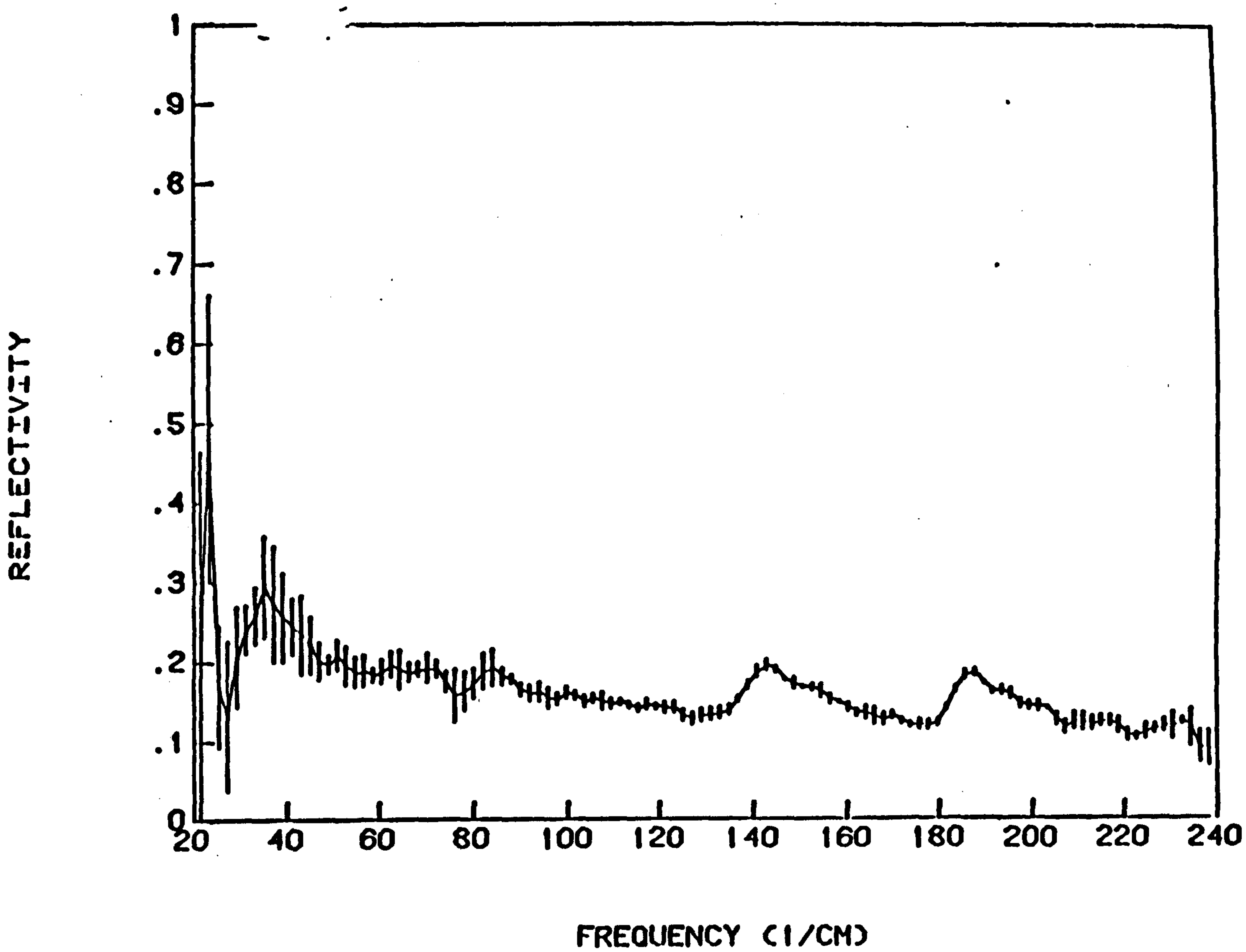

Figure 11. Room temperature far-infrared reflectance of CdMnTe grown on glass under the same conditions.

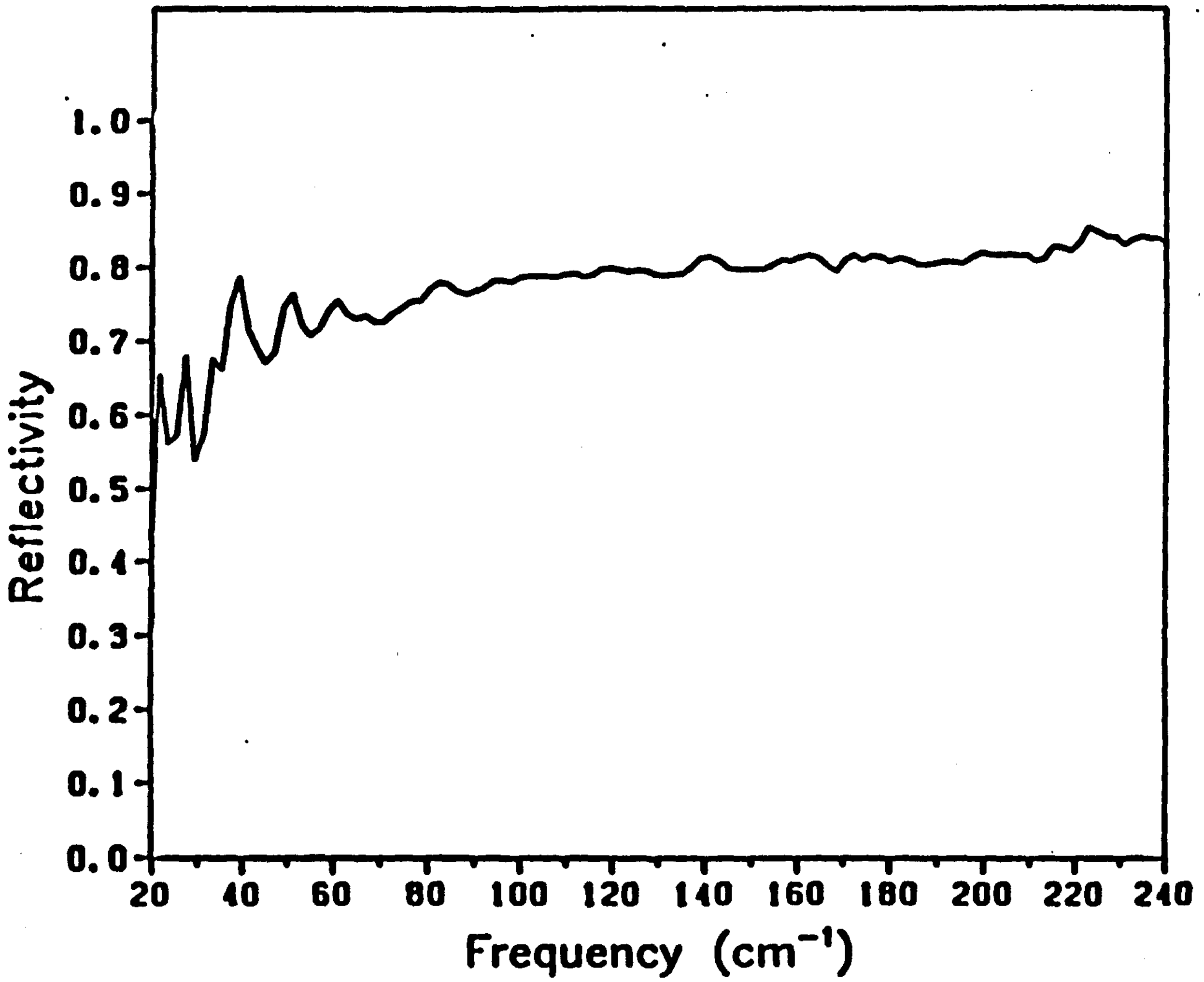

Figure 12. Room temperature far-infrared reflectance of CdMnTe grown on n-CdS film under the same conditions.

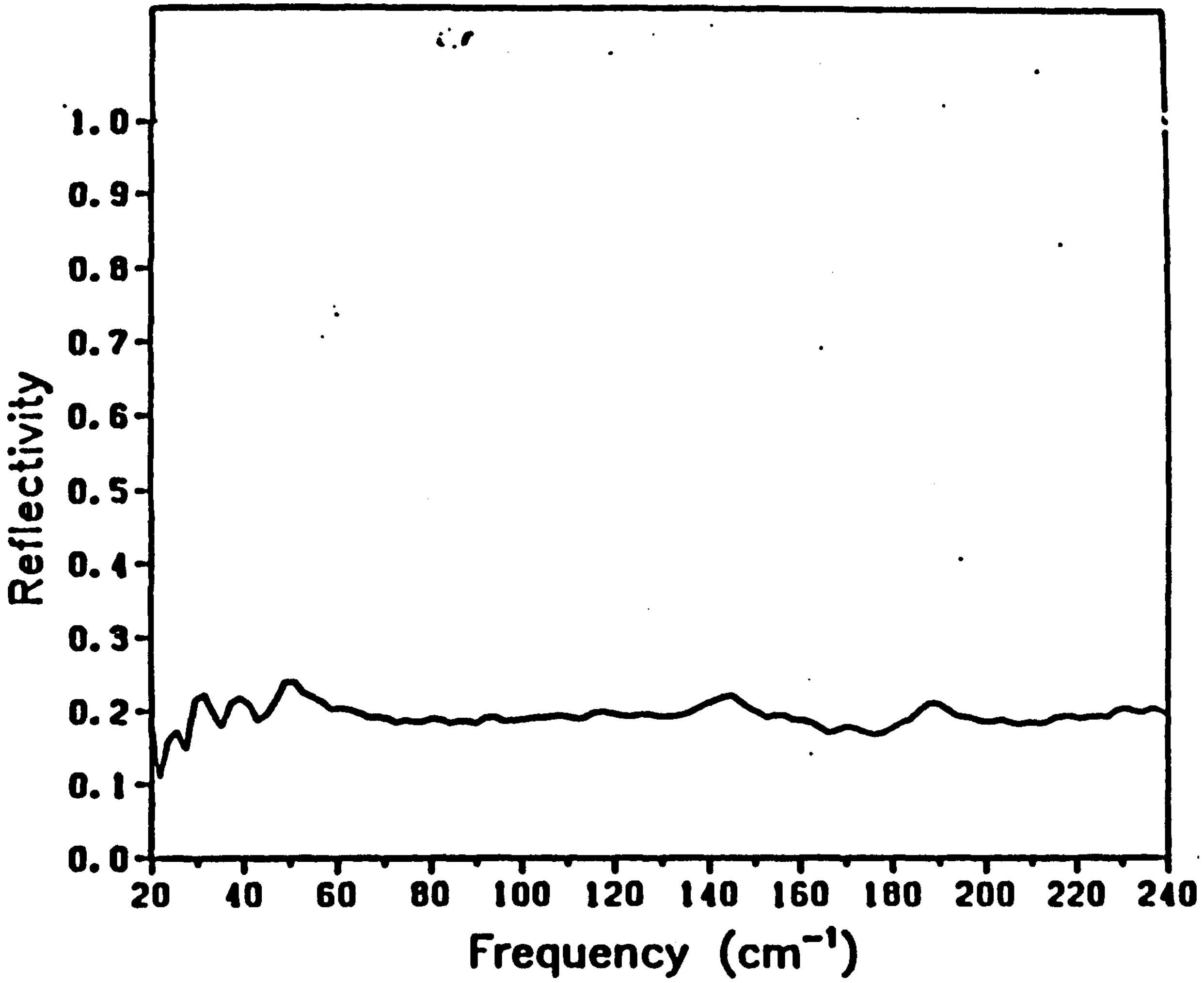

Figure 13. Room temperature far-infrared reflectance of CdMnTe grown on GaAs substrates under the same conditions.

GaAs, glass, and heavily doped CdS films respectively. It is clear from the figures that the shape of reflectance is different, which suggests that the quality may be different.

Non-destructive IR measurements were performed on poly films to estimate the thickness. IR measurements were made within the wavenumber range of 450-4000 cm^{-1} using Digilab FTS-40 Rapid scan interferometer with a resolution of 2 cm^{-1} at room-temperature. The thin film thickness was determined by $t = f/2n\omega$ where n is the index of refraction, ω is the wavenumber at which f-th maximum lies. For thick films ($t > 1.5$ um) with many fringes, the thickness can be estimated by $t = f/2\ n\Delta\omega$ where f is the number of extrema in the wavenumber interval ($\Delta\omega$) with average index of refraction n.[10] Figures 14 and 15 show the IR spectra of a thick and a thin film. In calculating the thickness, we assumed that the refractive index of CdMnTe is same as that of CdTe, since the variation in the high frequency dielectric constant ($\epsilon_{\infty} = n^2$) is small. We estimated the film thickness of samples A1112871 and A0217881 as 2.8 and 1.12 um respectively. The estimated thickness agrees well with the Alpha-step measurements.

2.24 Photoluminescence Measurements (PL)

PL measurements were performed, excited by Ar^+ 488 nm laser line, using a triple monochromator and a cooled optical multichannel analyzer. All measurements were done at 80 K. Figure 16 shows the PL spectrum of one of the CdMnTe films. The peak position gives a bandgap of 2.005 eV at 80 K. Using the relation $E_g = 1.58 + 1.51\ X$, we obtained Mn content of 0.28. Table 5 gives the bandgap values of some of the CdMnTe films.

Figure 17 shows Raman spectra of different batch of CdMnTe films grown at different substrate temperatures. In Raman spectra, it is known that appearance of sharp phonon peaks and higher order phonon peaks indicate good quality films. The Raman spectra show several sharp phonon peaks; the peaks at 167 and 205 cm^{-1} correspond to CdTe-like and MnTe-like first order longitudinal optic phonon modes. The peaks above 250 cm^{-1} correspond to higher order phonon modes. Below 400°C the Raman spectra show sharp phonon peaks and higher

TABLE 5. DATA FOR REPRESENTATIVE SETOF CMT FILMS GROWN BY MOCVD ON VARIED SUBSTRATE STRUCTURES. T_s SUBSTRATE TEMPERATURE DURING GROWTH; PL PEAK, ENERGY OF MAIN PHOTOLUMINESCENCE PEAK, GIVING THE BAND GAP AT 80K; x, FRACTION OF MN AS DETERMINED FROM PL PEAK

Sample	Substrate Structure	T_s (°C)	PL Peak (eV)	x
A0203882	GaAs	380	1.75	0.11
A1001872	GaAs	400	1.70	0.10
A0208881	GaAs	420	1.999	0.28
A0203881	GaAs	430	2.008	0.28
A0211881	GaAs	450	2.032	0.30
A0929871	GaAs	420	1.996	0.28
A0425871	CdTe/GaAs	420	2.005	0.28
A0925871	CdTe/GaAs	420	2.146	0.37
A1113871	CdS/SnO_2/glass	420	2.014	0.29
A0216881	glass	420	2.042	0.31

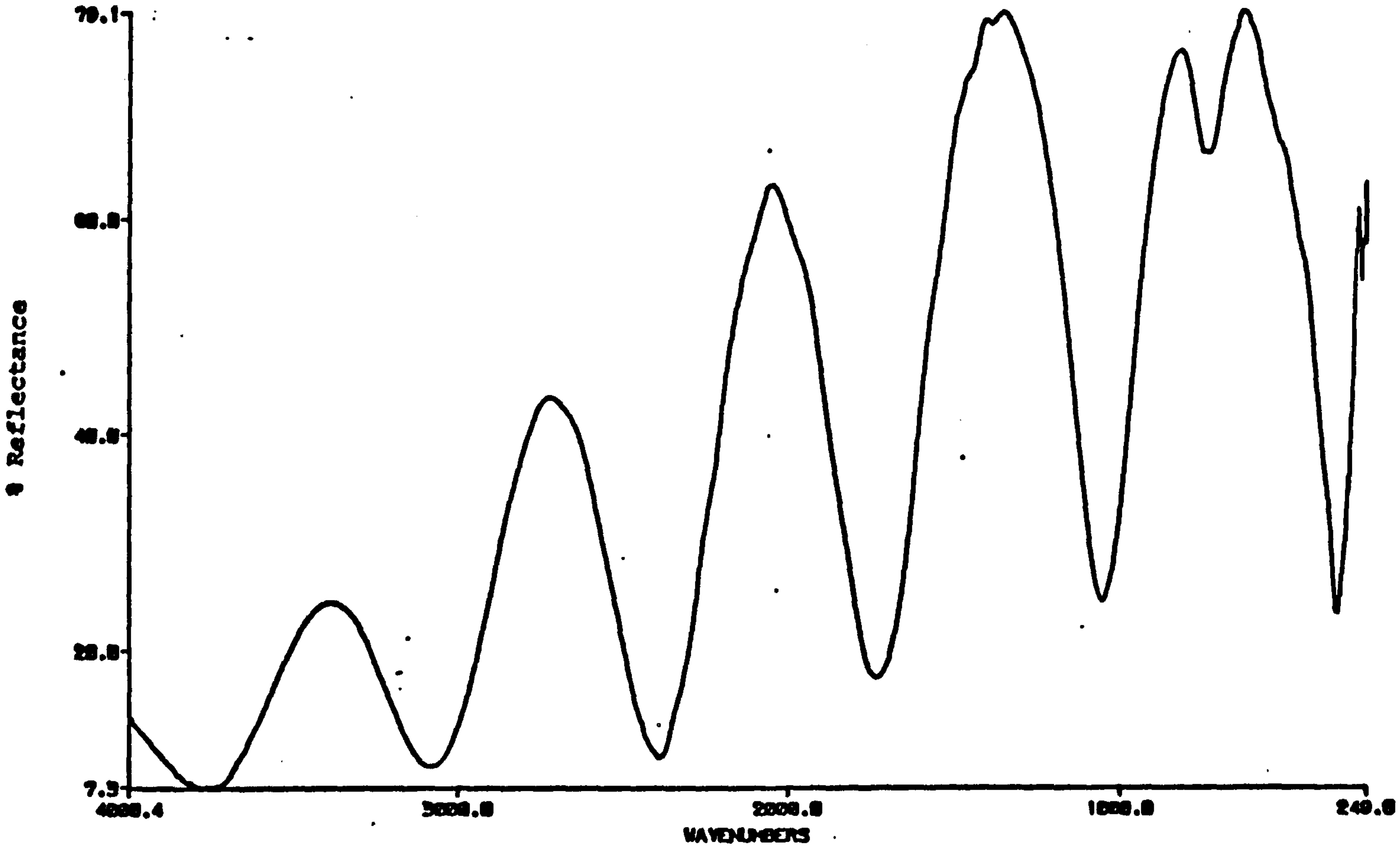

Figure 14. IR reflection spectrum of thick sample (A1112871).

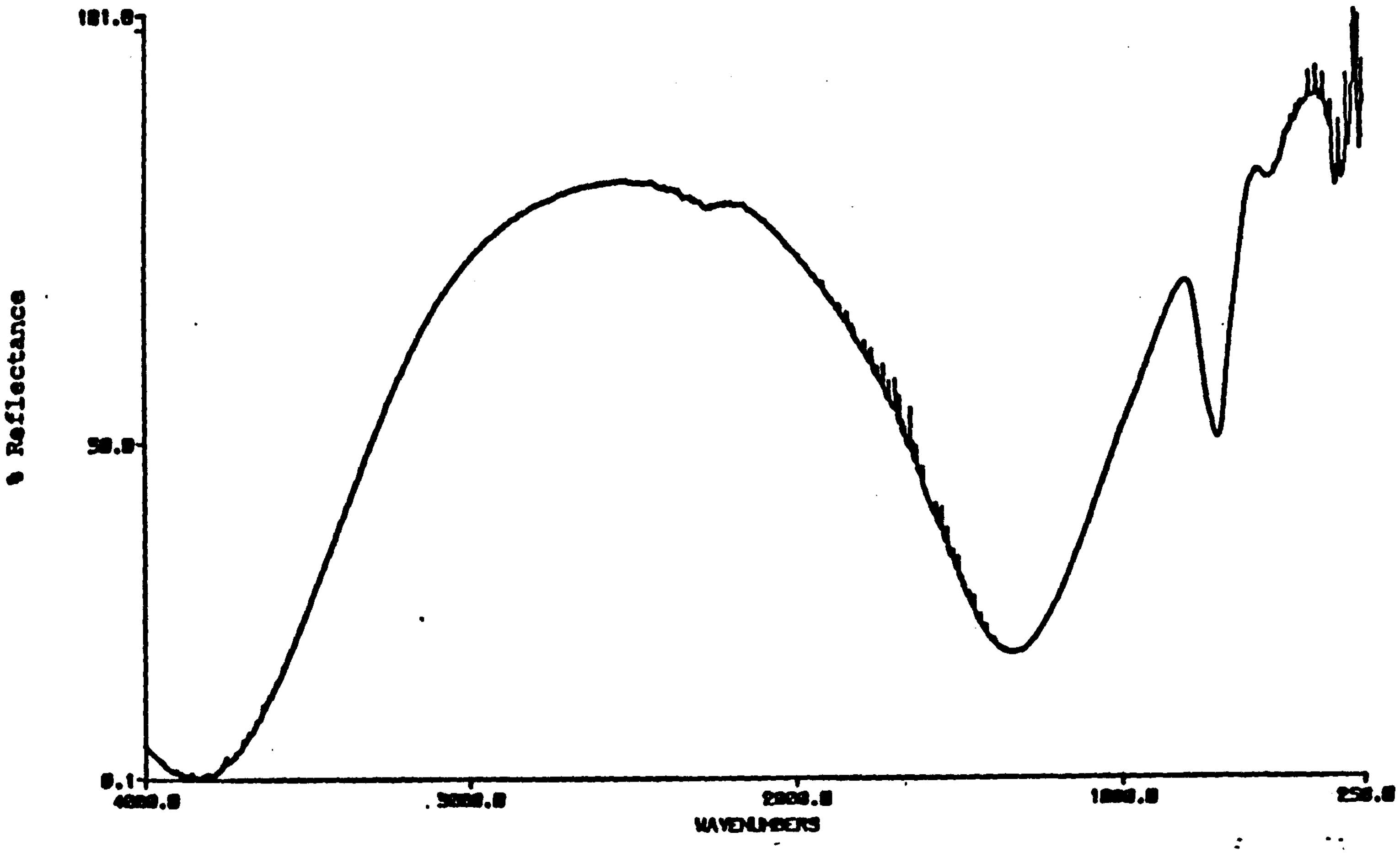

Figure 15. IR spectrum of thin sample A0217881.

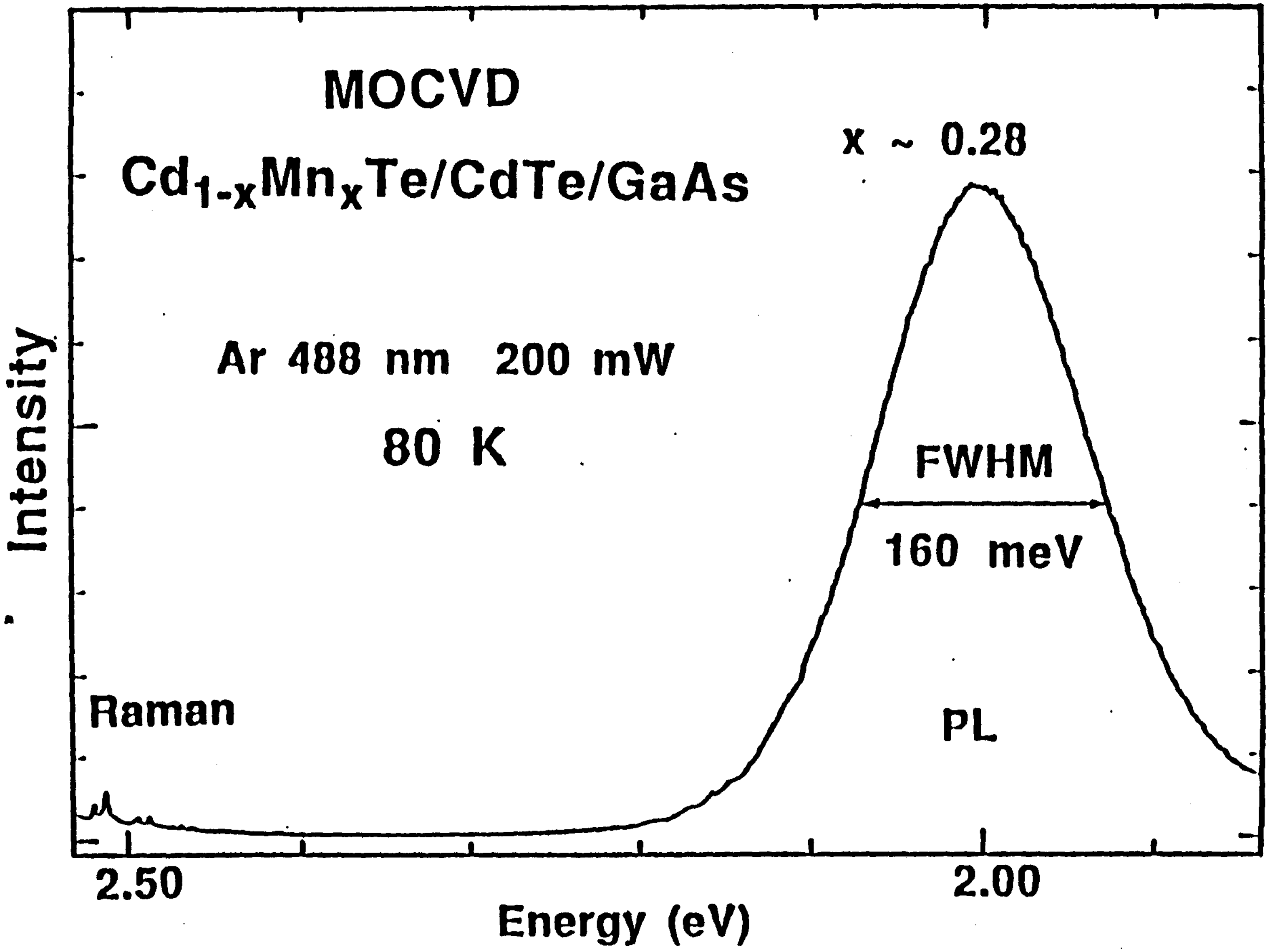

Figure 16. PL spectrum of polycrystalline sample A1113871.

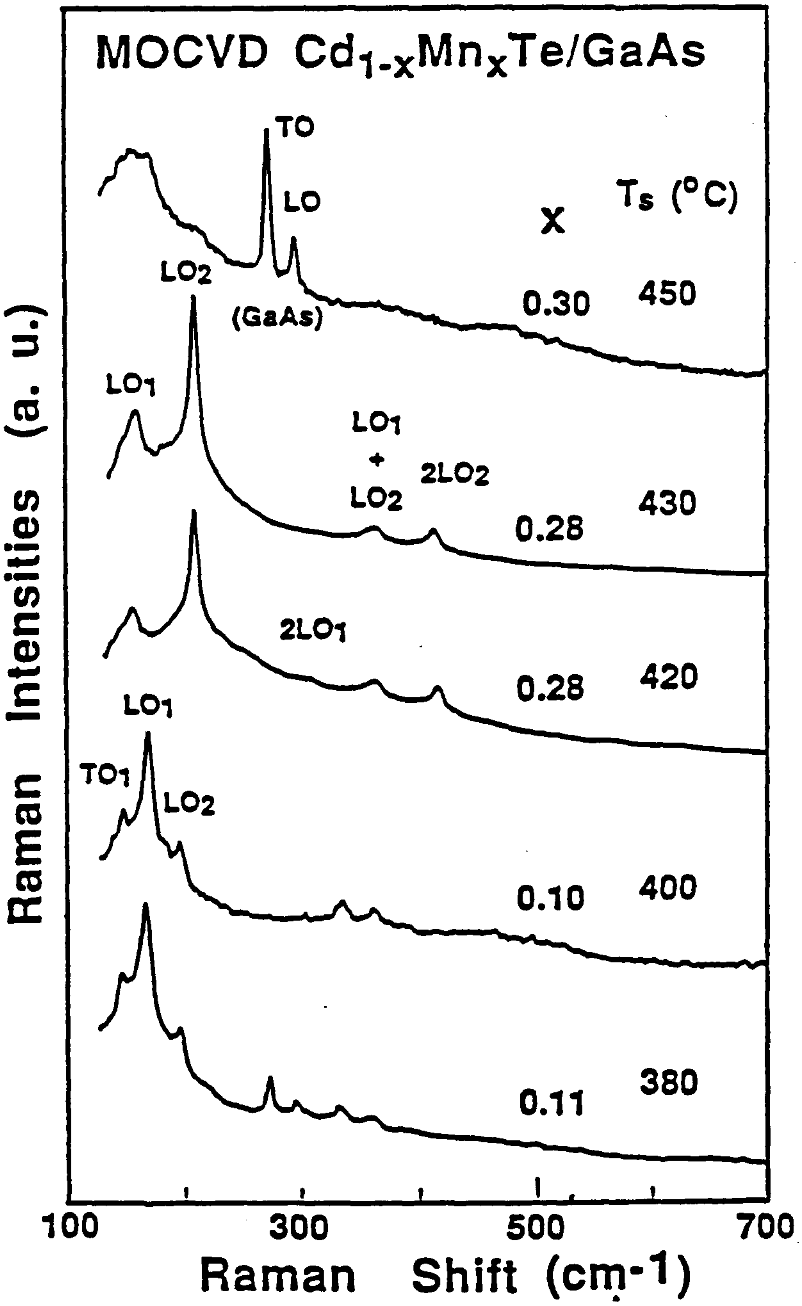

Figure 17. Raman spectra of single crystal CdMnTe films grown at different substrate temperatures.

order phonon peaks. This suggests that the quality of films is good but the Mn concentration is less than 10% (Mn concentration was estimated from PL measurements). This result agrees well with the IR results. At 420°C substrate temperature, the Raman spectra indicate good quality film. The disappearance of higher order phonon modes at 450°C indicates poor quality. Consistent with IR findings, PL measurements also showed increased incorporation of Mn at growth temperature greater than 400°C.

2.25 Auger Electron Spectroscopy (AES)

Auger depth profile measurements were done to investigate the film composition, uniformity, and the interface quality between Cd(Zn,Mn)Te and CdS films. AES was done on a Physical Electronics Model 600 Scanning Auger Multiprobe. All AES data was taken using a 3 KeV electron beam with a current of 1.0 uA. Auger depth profiles were taken by alternatively collecting data and sputtering with a rastered beam of 2 KeV Ar^+ ions. Figures 18 and 19 show the Auger depth profile of CdTe and CdMnTe films on CdS/SnO_2/glass substrates. The Cd and Te concentrations are uniform and flat in CdTe film, suggesting homogeneous composition of CdTe whereas in the case of CdMnTe film, the Cd, Te, and Mn concentrations are not uniform suggesting compositional inhomogenity. These Auger depth profiles correlate well with the sharp and broad absorption edges observed in the CdTe and CdMnTe spectra, respectively.

We find that the CdMnTe/CdS interface is broad and has Mn accumulation in the CdS region. The broad interface may be due to interdiffusion of CdTe and CdS films which may occur due to the combination of high growth temperature (400°C) and slow growth rate of CdTe film by MOCVD. In addition to performing depth profiles, specimens were fractured in atmosphere and immediately placed in the AES spectrometer for point analysis on the film fractured cross sections. This was done to avoid possible artifacts due to sputtering and to confirm the depth profile results of an apparent Mn accumulation near the interface of MOCVD grown CdMnTe. The compositions of the fractured film across sections at several points lying on apparent straight lines normal to the specimen surfaces were analyzed. A 10

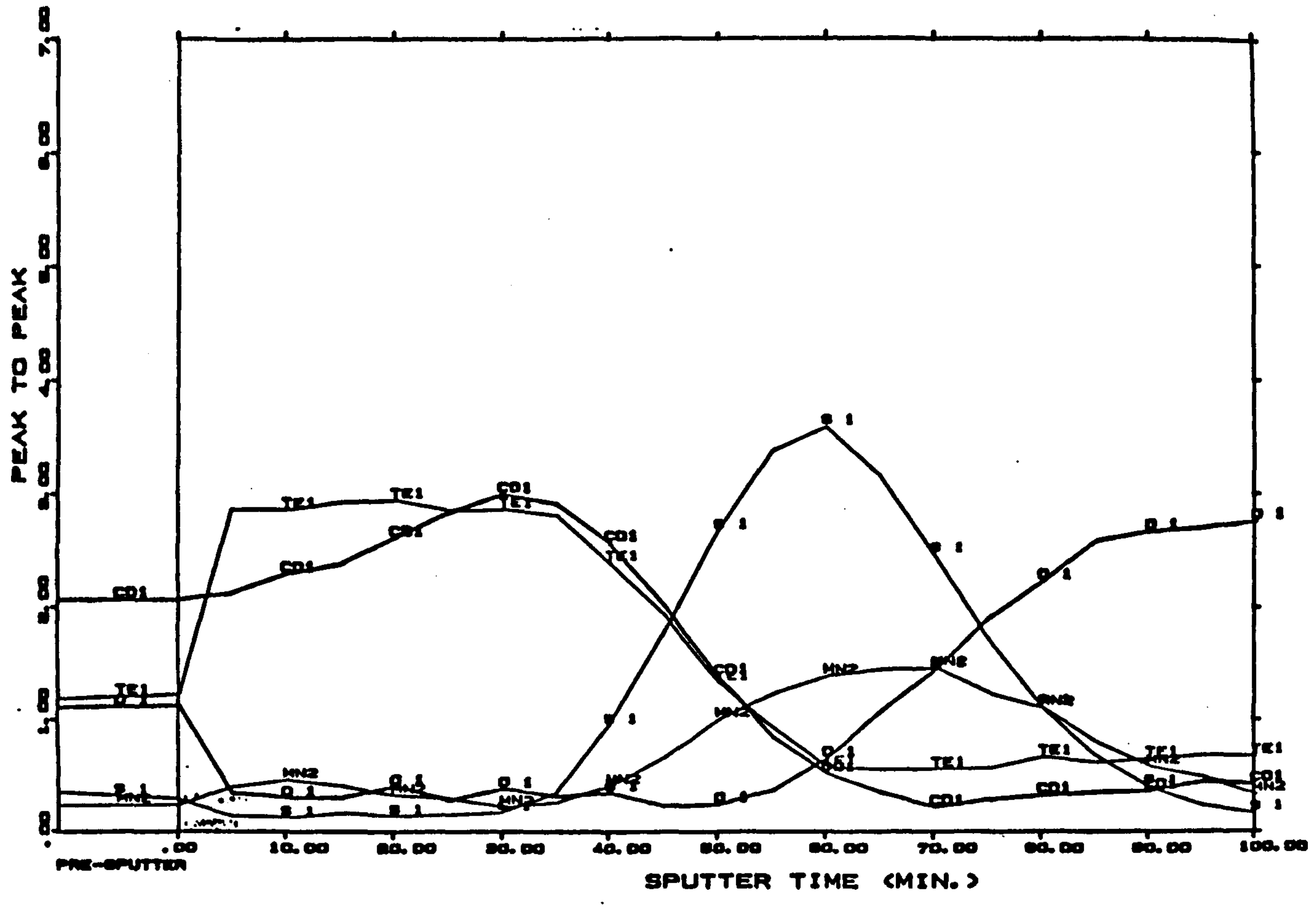

Figure 18. Auger depth profile of MOCVD grown polycrystalline CdMnTe/CdS film.

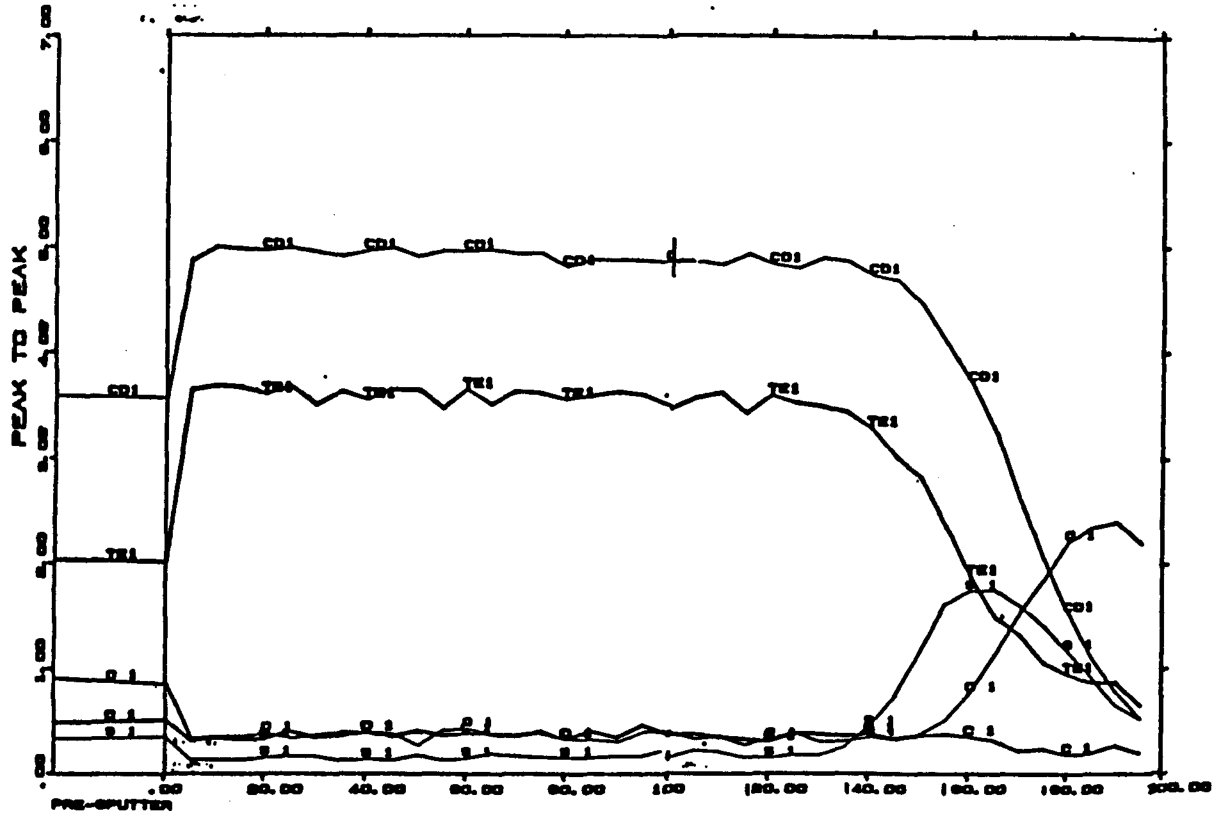

Figure 19. Auger depth profile of MOCVD grown polycrystalline CdTe/CdS film.

KeV electron beam of about 5 nA was used for these analyses in which the beam was approximately normal to the fracture surface. These measurements clearly indicate the presence of Mn at the interface and eliminated the possibility of sputtering artifact in depth profile analysis. Also, the depth profile analysis showed that the chemistry of Mn at the interface and in the film is different.

Auger depth profile analysis on single crystal CdMnTe grown as GaAs (111) simultaneously, showed no Mn accumulation at the interface (Figure 20), suggesting that the interdiffusion of CdS and CdMnTe films is the cause of accumulation of Mn at the interface. Further measurements are necessary to understand the mechanism of interdiffusion, which may involve Cd from CdS.

2.3 Processing of CdMnTe, CdZnTe Polycrystalline Films

Post deposition annealing in the presence of oxygen has been shown by a number of groups [11,12] to (i) cause a change in conductivity to p-type in as-grown CdTe and (ii) improve the quality of the CdTe/CdS heterojunction used in these solar cell structures. This effect has been well documented for CdTe grown by a variety of methods such as electrodeposition, close space vapor transport, etc., but annealing had not been attempted previously for MBE or MOCVD films, particularly ternary compounds such as CdZnTe and CdMnTe.

Anneals were performed in the range of 375-450°C for 30 min. The lower bound of 375°C was chosen since films which were earlier annealed at 325-375°C gave poor cells. Since oxygen was shown to be a necessary component in the CdTe process, the annealing was performed in laboratory (cleanroom) air. One anneal was done in an Ar ambient to confirm the necessity of oxygen. Figures 21-23 show Auger depth profiles of MBE as-grown CdTe, 2.7 um thick (E88-7), CdZnTe, 2.9 um thick (E88-8), and CdZnTe:Sb, 1 um thick (R88-1) films indicating excellent compositional uniformity and interface clarity in each case. The thicknesses of these films were found by IR measurements as described earlier. The atomic con-

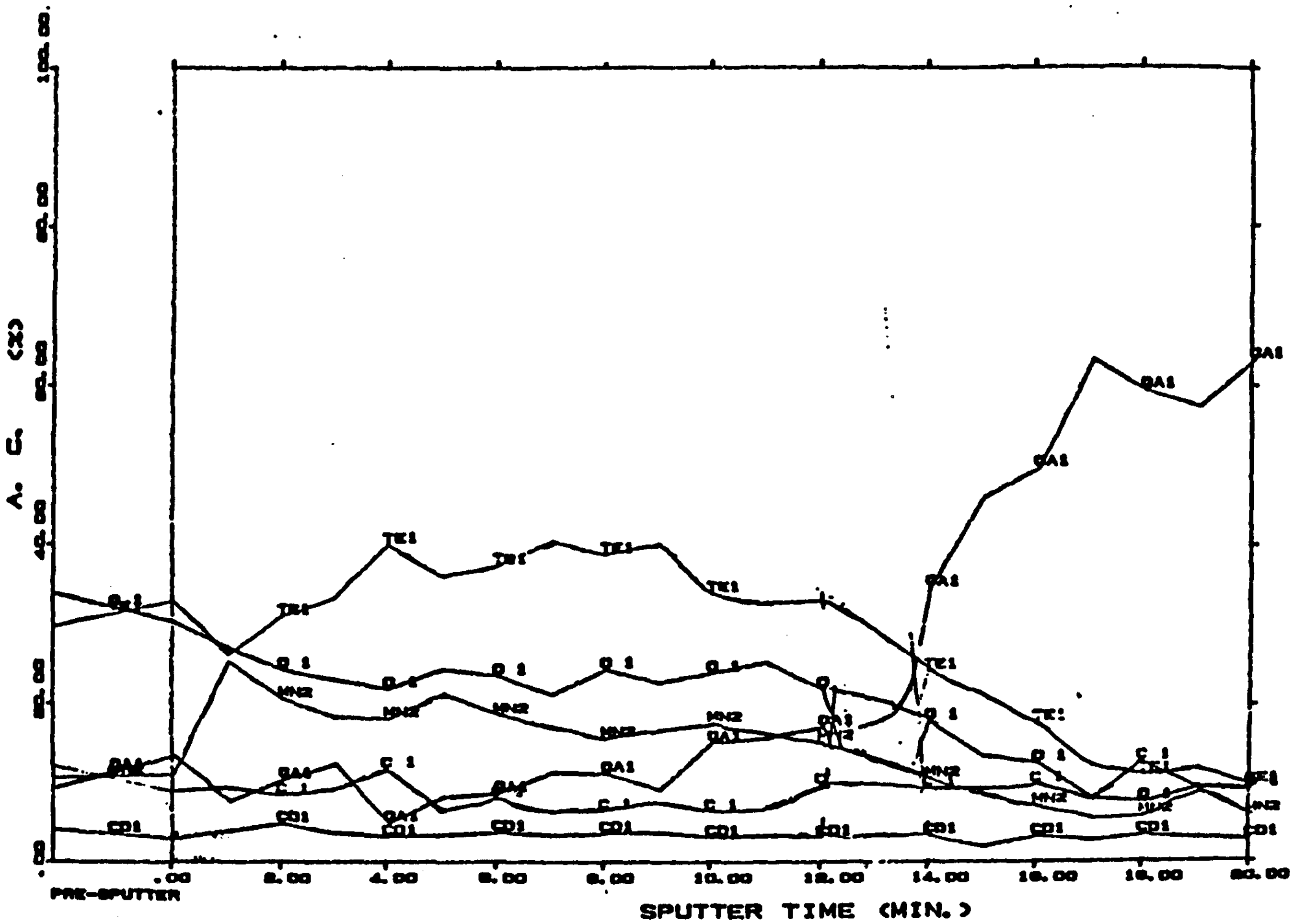

Figure 20. Auger depth profile of MOCVD grown single crystal CdMnTe/GaAs film.

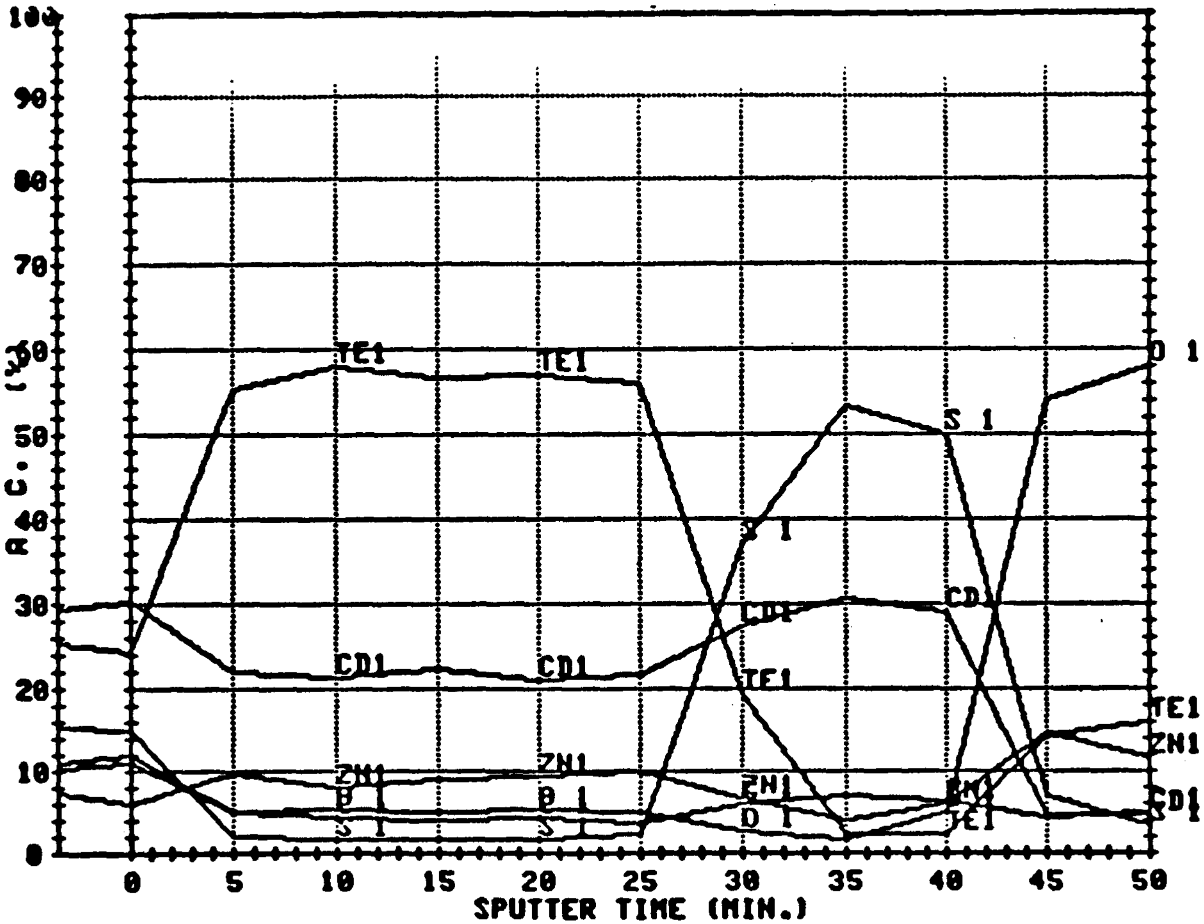

Figure 21. Auger depth profile of MBE grown polycrvstalline CdZnTe:Sb on CdS/SnO_2/glass substrate. CdZnTe:Sb film thickness is ~1 μm.

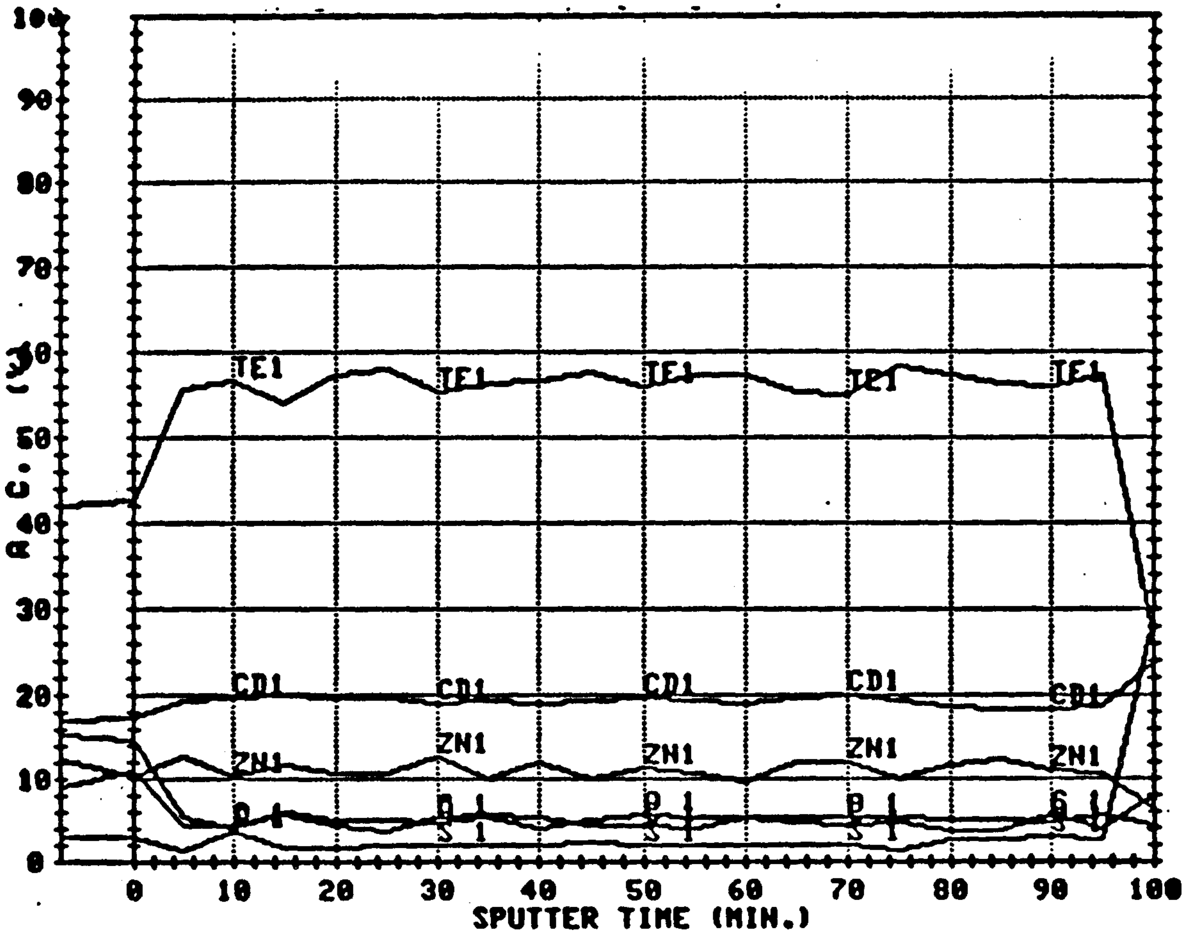

Figure 22. Auger depth profile of MBE grown polycrystalline CdZnTe on CdS/SnO$_2$/glass substrate. CdZnTe film thickness is ~2.9 μm.

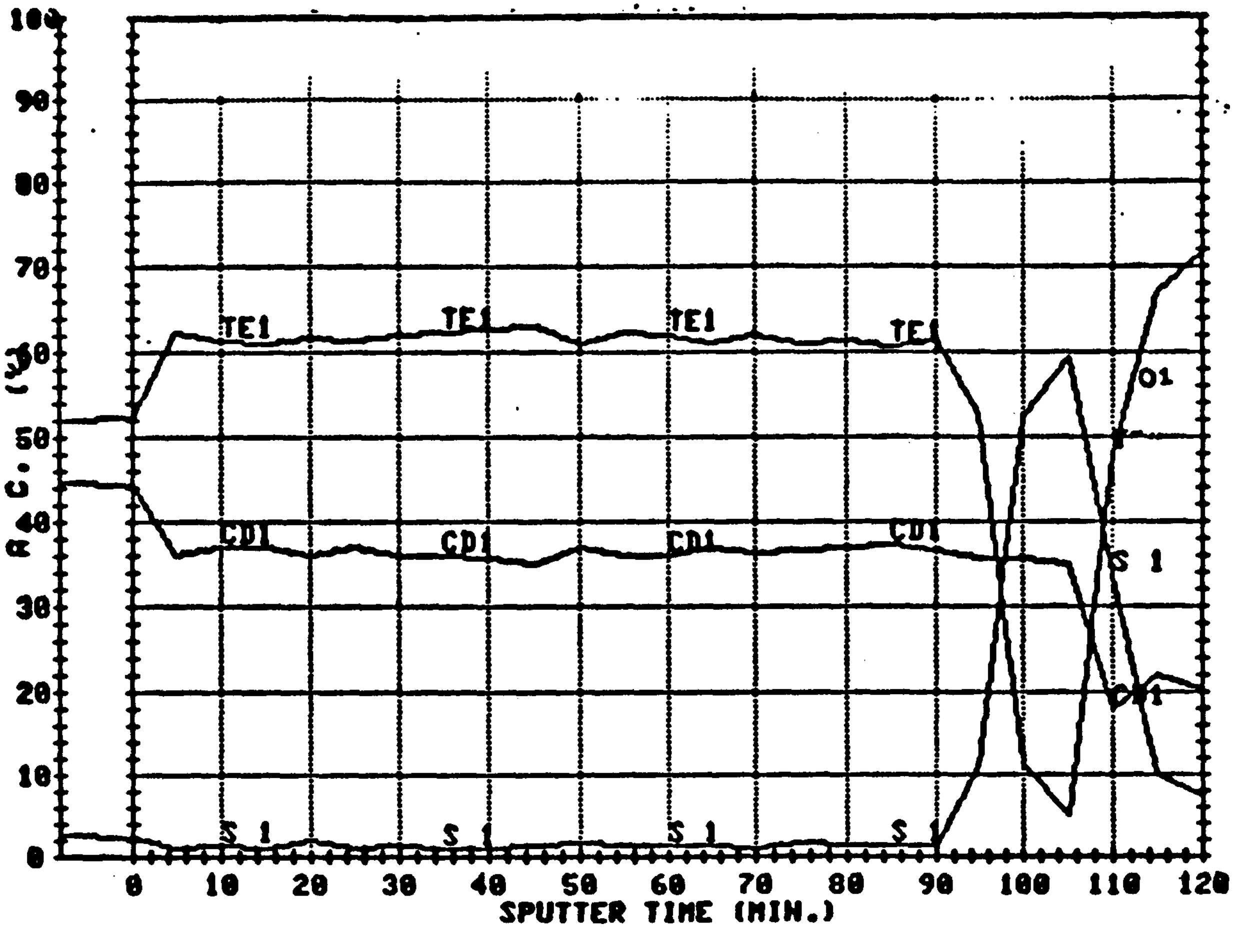

Figure 23. Auger depth profile of MBE grown polycrystalline CdTe on CdS/SnO_2/glass substrate. CdTe film thickness is ~2.7 μm.

centration values are in error here since correct sensitivity factors for CdTe and CdZnTe are presently not available.

Figure 24 shows the effect of annealing at the indicated temperatures for 30 min in air in the E88-8 CdZnTe film. Note the increasing response with temperature from no anneal to 425°C with the bandgap, and hence film composition, remaining constant. In addition, the relatively poor cutoff edge of the unannealed sample is straightened considerably, indicating fewer sub-bandgap defects present. The variations in the SPV responses were not found to be a result of thickness differences between the samples after the anneals since IR measurements taken immediately after the anneals indicate the thickness did not change. All of these observations strongly suggest that the SPV response magnitude is proportional to the bulk material quality. In contrast, the 410°C anneal response is drastically altered, with the response magnitude significantly reduced, the bandgap shifting toward that of CdTe, and a broadening in the edge itself. IR measurements show that the thickness of this film decreased to 2.5 um indicating the evaporation of the film. Thus, Figure 24 indicates that the optimal annealing temperature for maximum SPV repsonse and band edge abruptness is 385°C. SPV measurements were also made on a sample annealed in Ar but the response had little or no change from the as-grown film. It should be noted that the SPV response is measured from the back of the device and probably tells little about the CdS/CdZnTe heterojunction itself.

Auger measurements were done on some of the annealed samples to determine if changes in uniformity occurred. Figure 25 shows the Auger depth profile of the E88-7 CdTe sample after 30 min 400°C air anneal. A large concentration of oxygen is present near the surface as well as a depletion of Te. The CdS/CdTe interface is slightly less sharp than the as-grown sample due to some Te diffusion but the compositional uniformity within the film is still quite good. In comparison to an electrodeposited 9% efficient CdTe solar cell grown by Ametek, Figure 26, the interface quality and compositional uniformity are similar, except that the Ametek film has a ZnTe cap layer that is present for the first 5 min of sputtering and it has a significantly smaller amount of oxygen in the Auger profile near the surface. The large

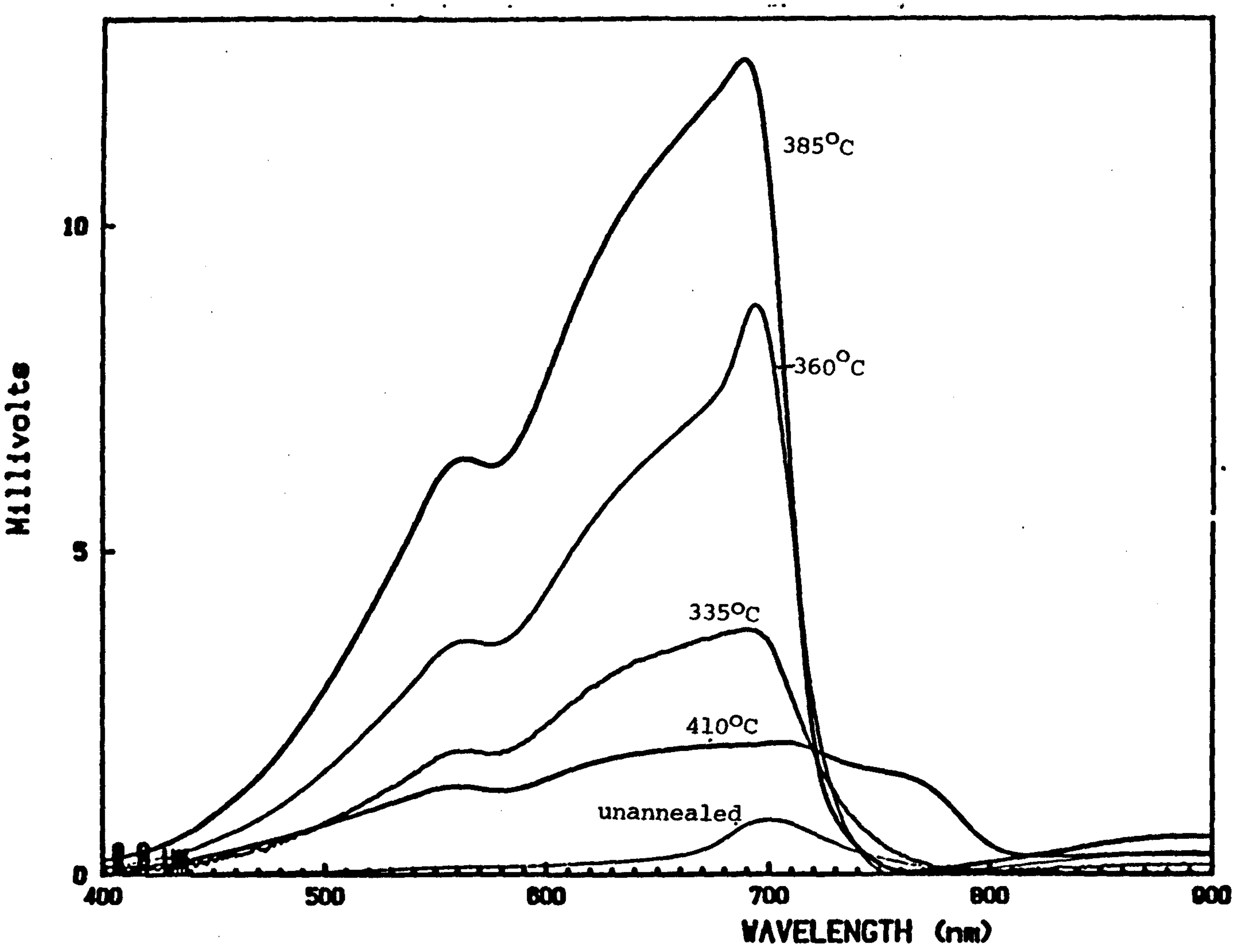

Figure 24. SPV spectra of E88-8 CdZnTe film annealed for 30 min. in air at indicated temperatures.

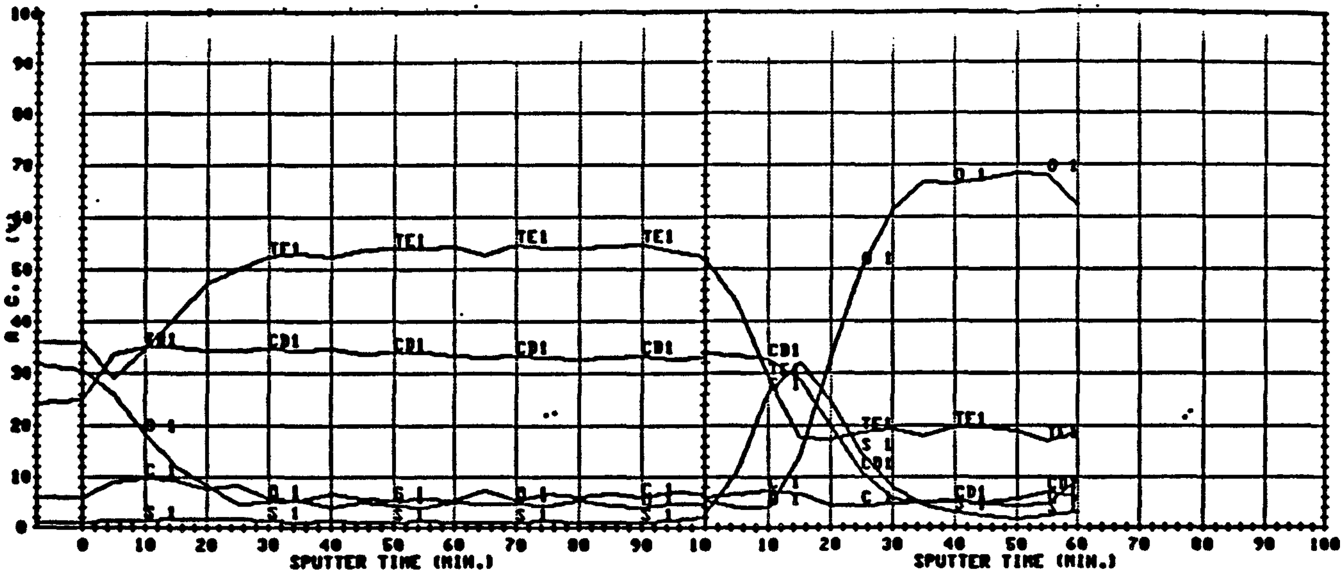

Figure 25. Auger depth profile of E88-7 CdTe film (Fisoil 1) after 30 min. 400°C air anneal.

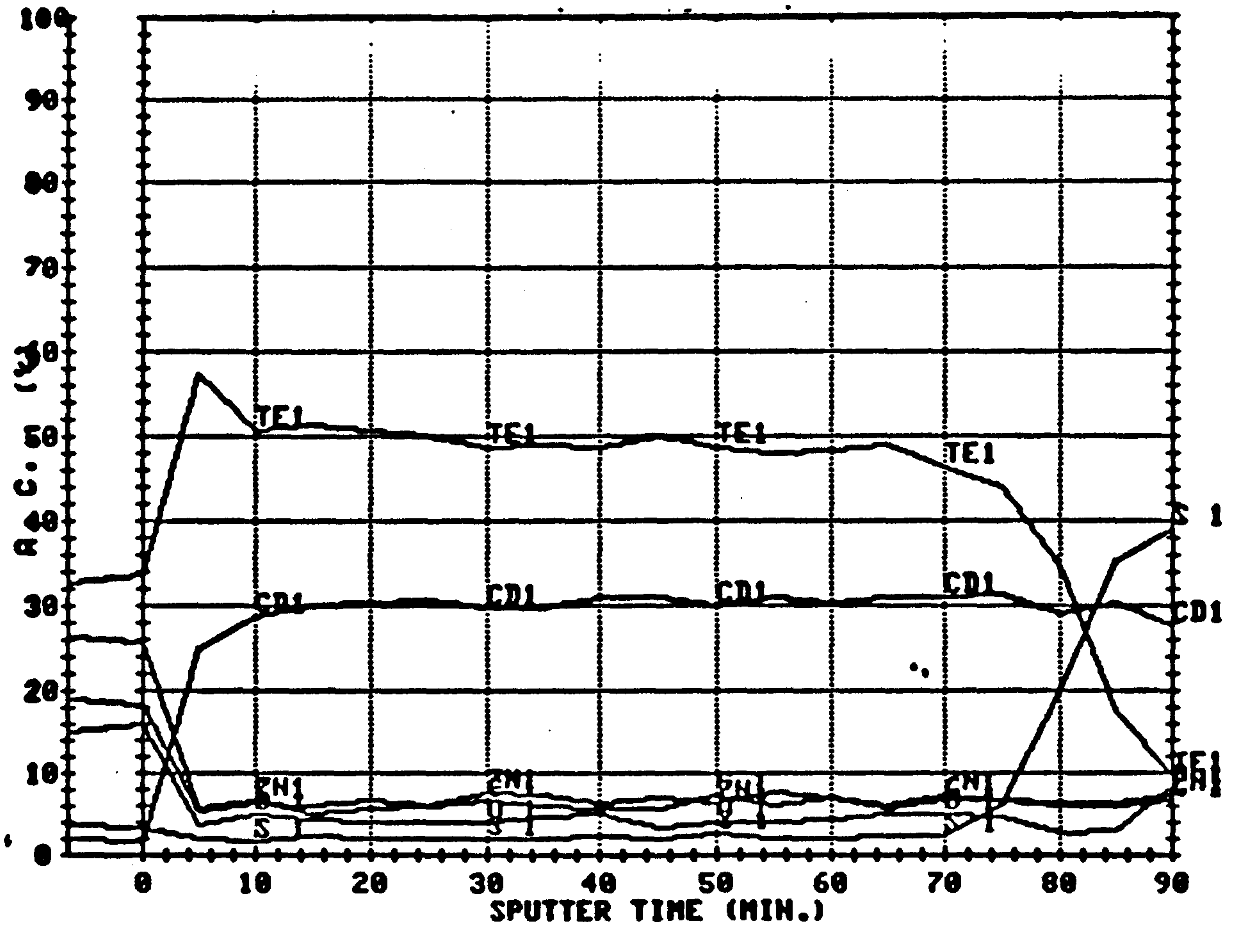

Figure 26. Auger depth profile of a 9% CdTe Ametek cell for comparison with our work.

amount of oxygen at the surface of our film was removed by a 5 min chemical etch in dilute buffered NaOH as indicated by further Auger profiling.

Four CdMnTe samples were used to investigate the effect of annealing in air. Samples were annealed at 200, 300, and 400°C in the forming gas for 30 minutes. Figures 27-29 show a comparison of SPV response before and after the annealing for each sample. It is interesting to note that 200 and 300°C anneal reduced the SPV response but 400°C anneal enhanced the SPV response. This suggests that 400°C anneal is the best for improving the quality of this film. Maximum SPV response increased by a factor of 2, from 10 mV to 20 mV, after 400°C. A 200°C anneal reduced the maximum response signal by a factor of 2, from 10 mV to 5 mV.

2.4 Device Fabrication and Measurements

2.41 CdTe Absorber Films

[***]CdTe films were grown by both MBE and MOCVD techniques on CdS/SnO_2/glass substrates to understand the film properties and solar cell characteristics. These films were annealed at 400°C for 30 min in breathing air followed by a mild etch of Bromine methanol before the vacuum evapoaration of ZnTe. A copper-doped p^+-ZnTe interlayer facilitates the back ohmic contact formation when nickel contacts were evaporated through a shadow mask with openings of 8 mm^2. Table 6 gives the CdTe solar cell device parameters grown by MBE and MOCVD.

2.42 CdMnTe Absorber Films

Thin films of CdMnTe grown at 420°C substrate temperature and thickness of 2 um were used for solar cell measurements. Cell fabrication was done in three parts: (a) without any anneal, (b) after 400°C/30min anneal, and (c) 400°C/30 min anneal followed by vacuum evaporation of p^+-ZnTe layer at 200°C.

[***] All solar cells were fabricated by Ametek Applied Materials Laboratory.

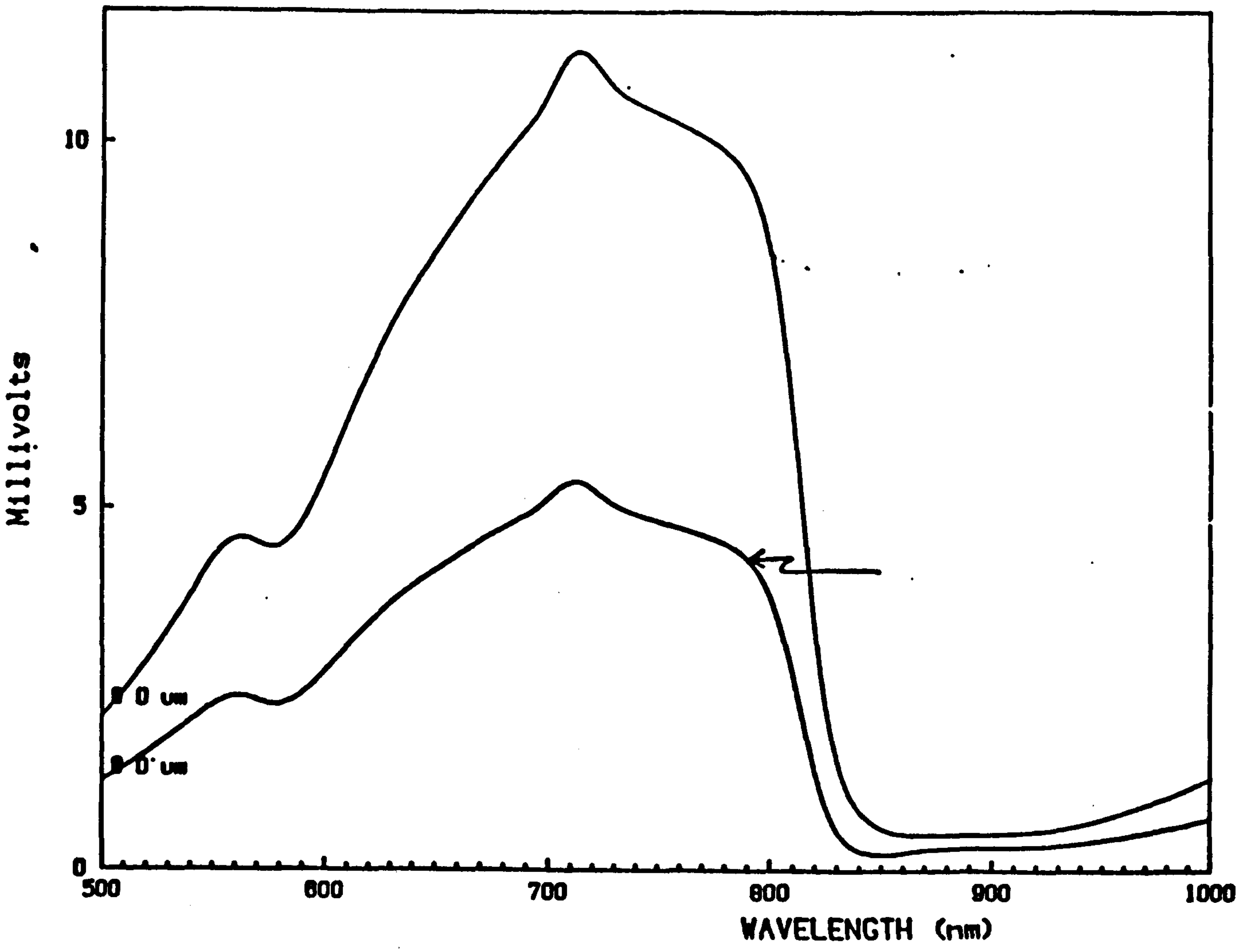

Figure 27. SPV response of Film A, before and after 200°C anneal in forming gas.

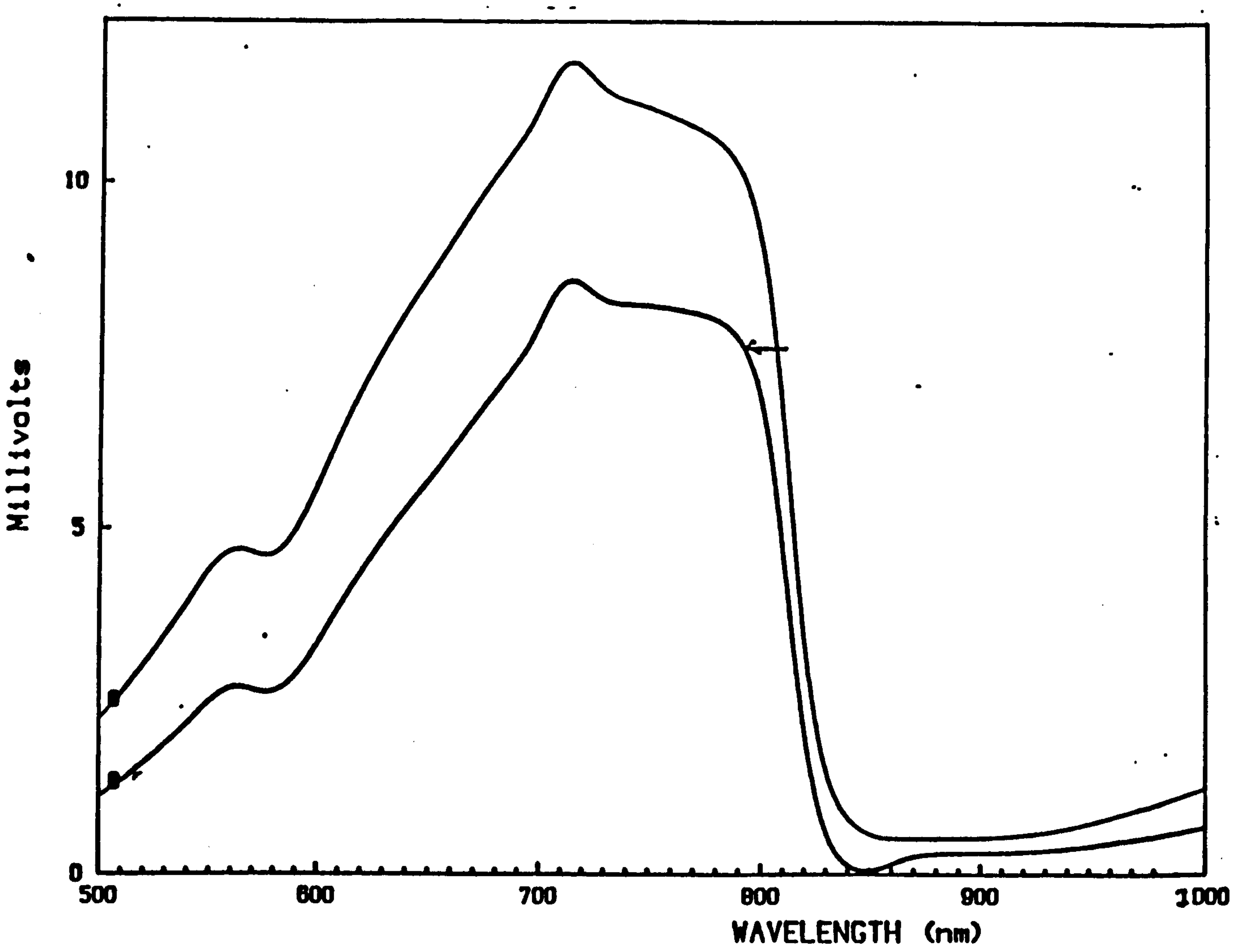

Figure 28. SPV response of Film B, before and after 300°C anneal in forming gas.

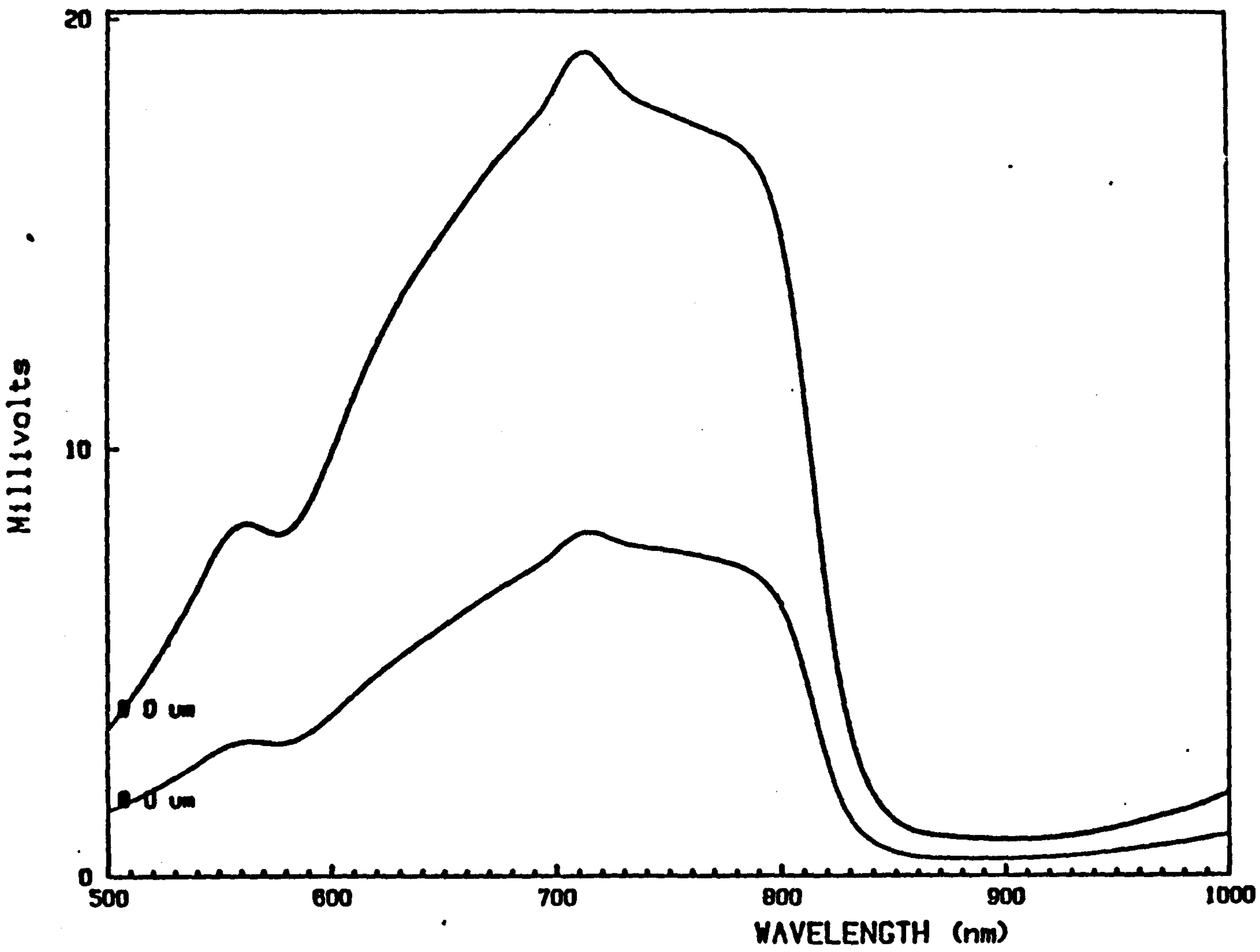

Figure 29. SPV response of Film C, before and after 400°C anneal in forming gas.

TABLE 6. DEVICE PARAMETERS OF MBE-GROWN CdTe AND CdZnTe SAMPLES.

Sample	Target Composition	Device Structure	Thickness (μm)	V_{OC} (volts)	J_{SC} (mA/sq cm)	FF	Efficiency
R87-44	$Cd_{.9}Zn_{.1}Te$	p-n	1.2	.434	11.5	.322	1.61
R87-44	$Cd_{.9}Zn_{.1}Te$	p-i-n	1.2	.370	14.4	.334	1.79
R87-46	CdTe:Sb	p-n	.7	.104	14.8	.2525	0.39
R87-46	CdTe:Sb	p-i-n	.7	.098	14.4	.250	0.35
R87-51	$Cd_{.75}Zn_{.25}Te$:Sb	p-n	1.15	.510	7.69	.241	0.95
R87-51	$Cd_{.75}Zn_{.25}Te$:Sb	p-i-n	1.15	.511	14.4	.484	3.6
R88-1	$Cd_{.75}Zn_{.25}Te$:Sb	p-i-n	1.10	.541	15.0	.41	3.3
R88-2	$Cd_{.75}Zn_{.25}Te$:Sb	p-i-n	1.10	.463	12	.36	2.0
E88-1	$Cd_{.75}Zn_{.25}Te$:Sb	p-i-n	2.5	.472	1.88	.27	0.21
E88-7	CdTe	p-n	3.0	.548	22.8	.522	6.54
E88-7	CdTe	p-i-n	3.0	.741	17.2	.56	7.6
R88-2	CdZnTe:Sb (with laser)	p-i-n	1.10	.317	13.3	.29	1.22

Solar cells fabricated on film with low Mn content ($x = 0.05$) gave cell efficiencies in the range of 6.0%-6.7%, with $V_{OC} = 680$ mV, $J_{SC} = 20.6$ mA cm^{-2}, and a fill factor (FF) of 0.442-0.500 (Figure 30). Dark I-V measurements (Figure 31) suggests that the low fill factor is due to excess junction leakage current. Figure 32 shows the spectral response of a 6.2% efficient CdMnTe cell when illuminated from the front (CdS) and the back (ZnTe). The data confirm that CdS-CdMnTe is indeed the collecting heterojunction since the front spectral response is much higher. The spectral response cut-off edge (about 810 nm) of the finished cell corresponds very well with the SPV cutt-off edge of the as-grown film. This indicates that the Mn content remains unchanged during the cell fabrication.

The annealing of CdMnTe film in air at different temperatures has a good effect on cell efficiency. We observed that SPV response of CdMnTe films increased with increasing annealing temperature from 200° to 400°C. The cell efficiency increased with increasing annealing temperature. Table 7 gives performance of CdMnTe solar cells annealed at different temperatures.

2.43 CdZnTe Absorber Films

Both p-i-n and p-n solar cells were fabricated using CdZnTe and CdZnTe:Sb films as absorber. Table 8 gives the CdZnTe solar cell parameters.

TABLE 7. PERFORMANCE OF CdMnTe SOLAR CELLS ANNEALED AT DIFFERENT TEMPERATURES.

Film ID	Annealing Temperature	Voc mV.	Jsc ma/cm^2	FF	%
B	Unannealed	393	2.99	0.438	0.52
D	300°C	456	4.02	0.382	0.70
C	400°C	488	7.96	0.353	1.37
A	200-400°C	421	9.82	0.326	1.35

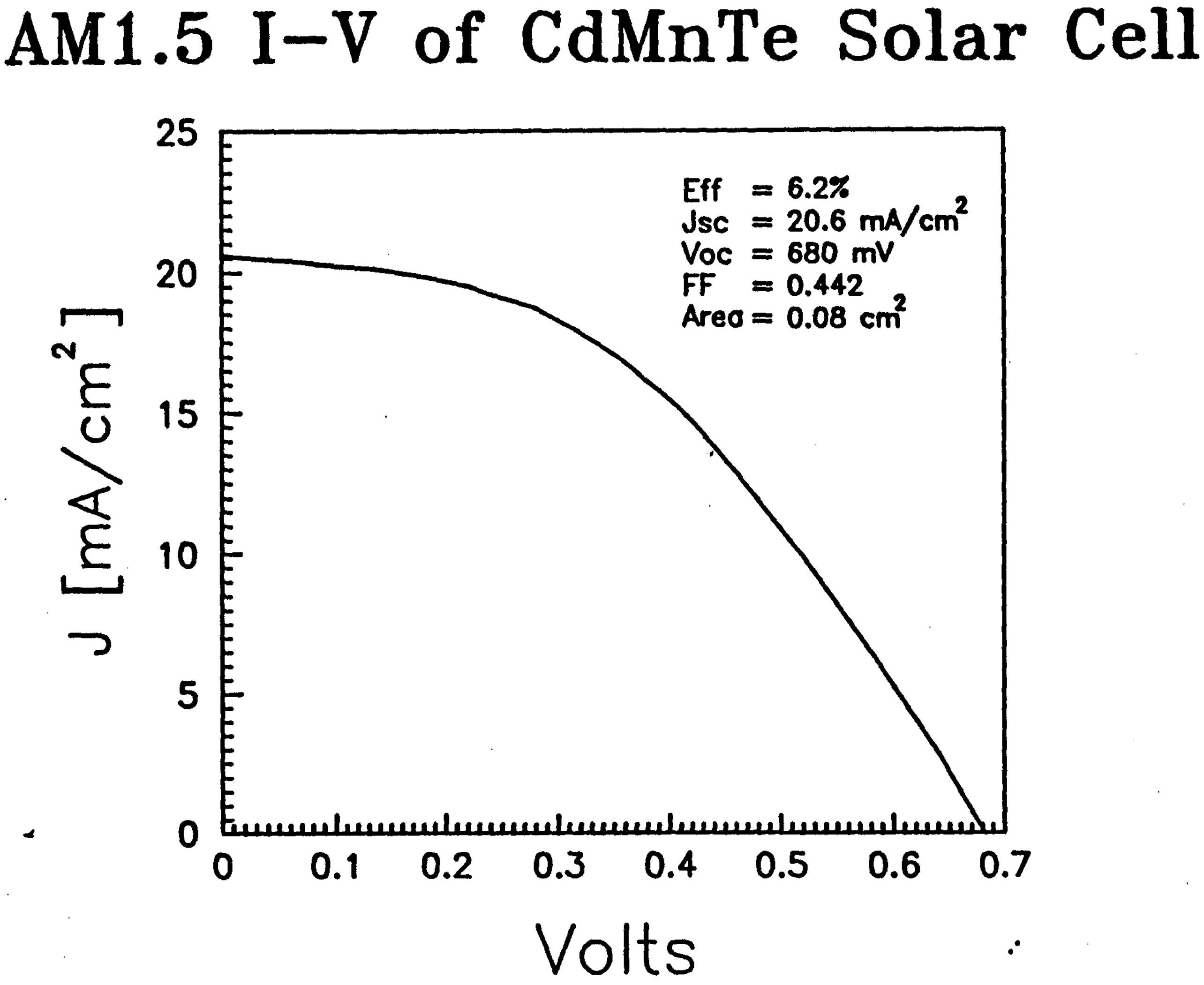

Figure 30. Illuminated I-V data of a 6.2% efficient polycrystalline CdMnTe cell: J_{sc} = 20.6 mA cm^{-2}; V_{oc} = 680 mV; FF = 0.442; area, 0.80 cm^2.

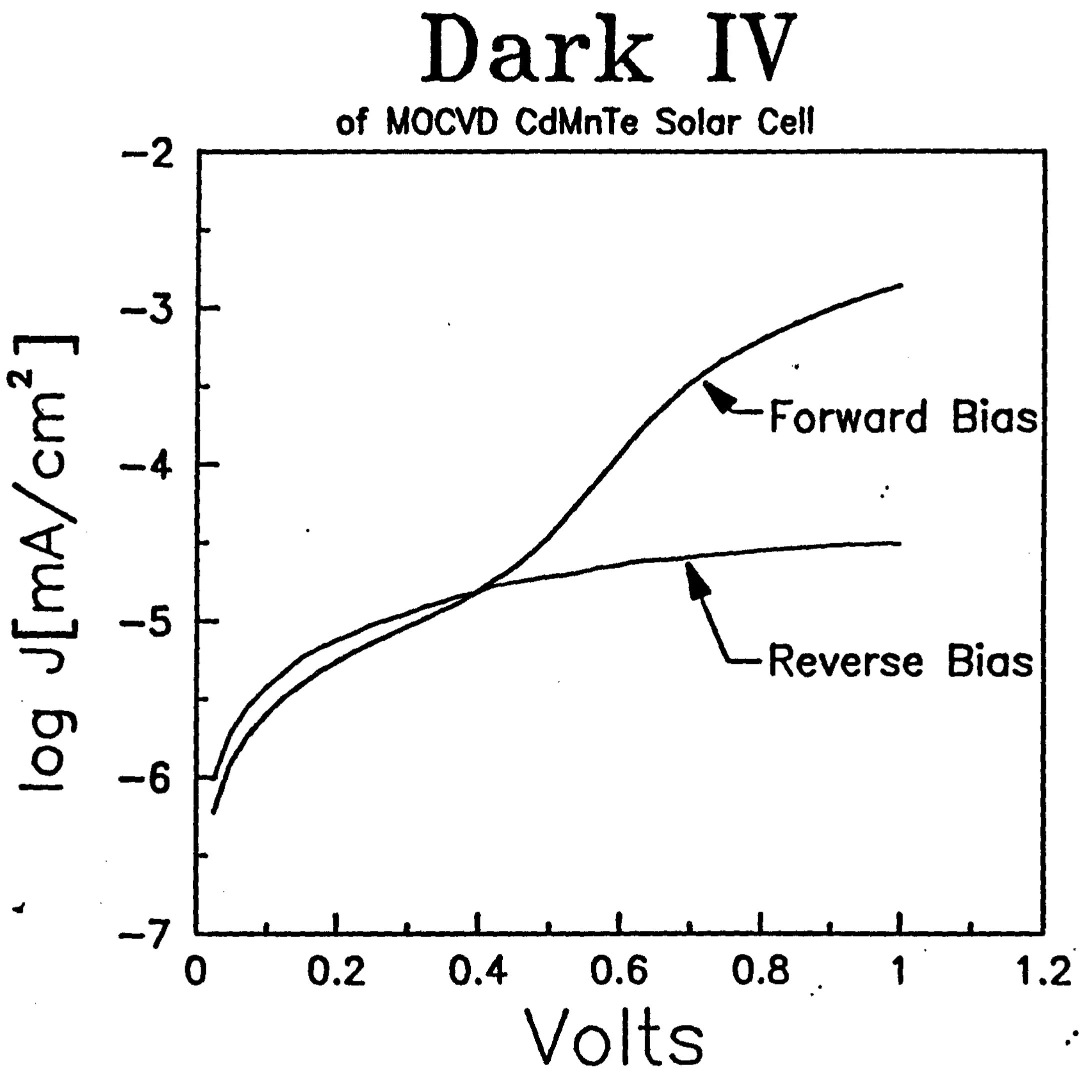

Figure 31. Forward and reverse dark I-V data for a 6.2% efficient CdMnTe cell.

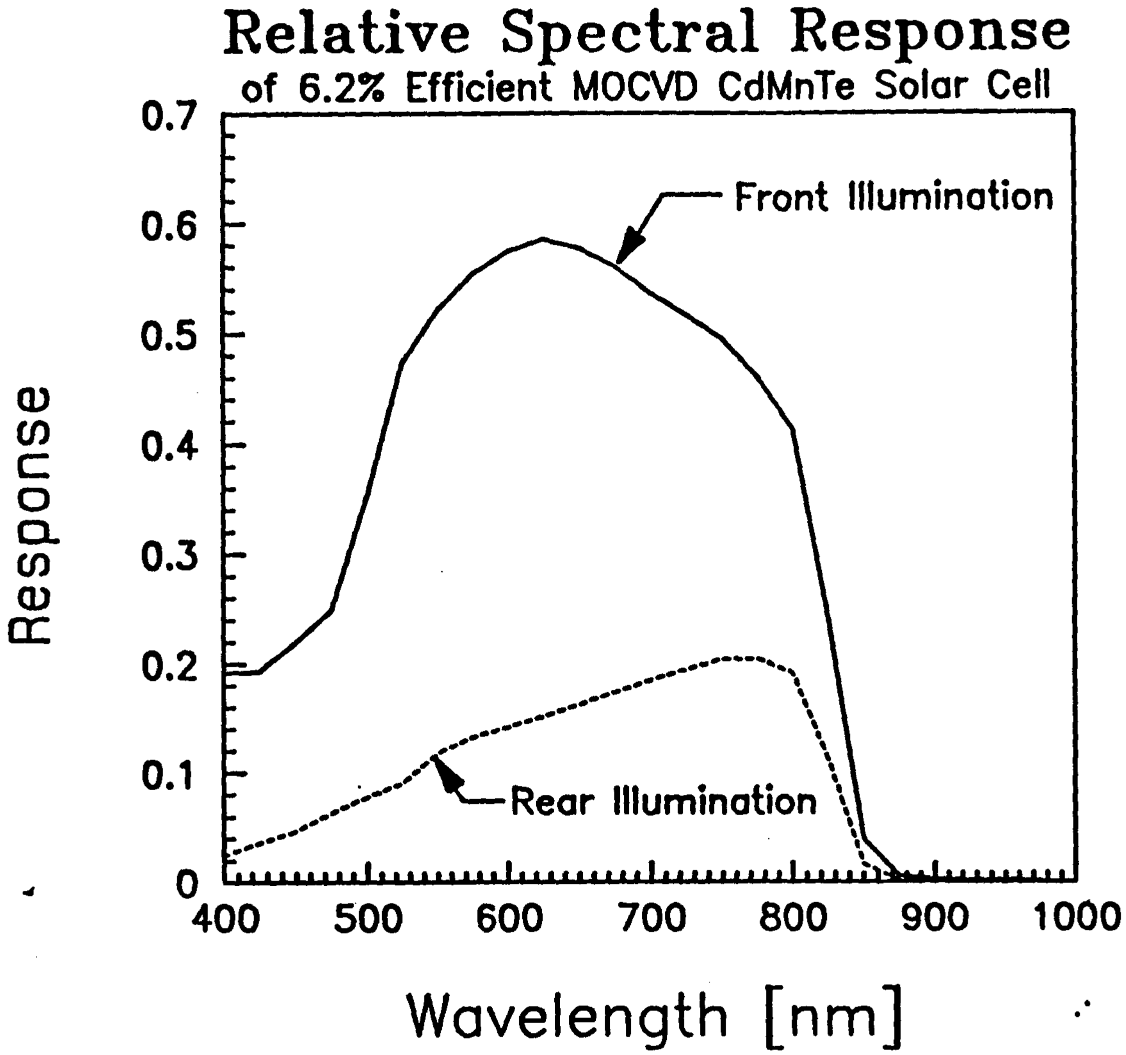

Figure 32. Spectral response of a 6.2% efficient polycrystalline CdMnTe cell.

3. CONCLUSIONS

Single and polycrystalline $Cd_{1-X}Mn_XTe$ (X = 0.0 - 0.30) films were grown by MOCVD. X-ray measurements indicated a single phase and the Mn values were estimated from the calculated lattice constant values. From surface photovoltage measurements we estimated the bandgap of the films which agreed well with the X-ray data. Infrared spectra taken on single crystal $Cd_{1-X}Mn_XTe$ films suggested that 420°C is an optimum substrate temperature for growing good quality films with Mn concentration greater than 20%. This gives the optimum bandgap 1.7 eV for solar cell applications. We estimated the thickness of polycrystalline films from IR measurements. Auger depth profile analysis showed that the composition of CdTe polycrystalline films is uniform and the interface is broader than MBE-grown CdTe. In the CdMnTe films the Auger results indicated that the bulk composition is not uniform and the interface has excess Mn probably due to interdiffusion of CdS and CdMnTe.

$Cd_{1-X}Zn_XTe$ (X = 0 - 0.30) polycrystalline films were grown by MBE. P-type doping was attempted by incorporating Sb into the film both with and without laser beam excitation. The composition and bandgaps were estimated using X-ray diffraction and surface photovoltage techniques. The presence of Sb in the films was verified by in-situ Auger measurements. The thickness of the film was estimated from IR spectra. The bulk composition of both CdTe and CdZnTe films were found to be uniform in contrast to MOCVD-grown CdMnTe film. The interface of CdS and CdTe, CdZnTe is sharp which is also different from CdMnTe and CdS interface.

Cell efficiencies in the range 6.0 - 6.7% were achieved on $Cd_{0.95}Mn_{0.05}Te$ film using the glass/SnO_2/CdS/CdMnTe/ZnTe/Au frontwall solar cell structure. Solar cells made with higher Mn content gave very low efficiencies, maybe due to nonuniformity in composition and poor interface quality. Solar cells fabricated using CdZnTe films gave 3.0-3.6% efficiencies.

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6. PRESENTATIONS AND PUBLICATIONS ON II-VI PROGRAM

Published Papers in Journals

1. A. Rohatgi, S. A. Ringel, J. Welch, E. Meeks, K. Pollard, A. Erbil, C. J. Summers, P. V. Meyers, and C. H. Liu, "Growth and Characterization of CdMnTe and CdZnTe Polycrystalline Thin Films for Solar Cells," *Solar Cells*, 24, 185-194, 1988.

2. Z. C. Feng, R. Sudharsanan, S. Perkowitz, A. Erbil, K. T. Pollard, and A. Rohatgi, "Raman Scattering Characterization of High-Quality $Cd_{1-x}Mn_xTe$ Films Grown by Metalorganic Chemical Vapor Deposition," *Appl. Phys. Lett.*, 1988.

3. A. Rohatgi, R. Sudharsanan, S. A. Ringel, P. V. Meyers, and C. H. Liu, "Wide Bandgap Thin Film Solar Cells from CdTe Alloys," *Proc. of 20th IEEE Photovoltaic Specialists Conference*, Las Vegas, NV, Sept. 26-30, 1988.

Submitted Papers for Publication

1. R. Sudharsanan, Z. C. Feng, S. Perkowitz, A. Rohatgi, K. T. Pollard, and A. Erbil, "Characterization of MOCVD-Grown CdMnTe Films by Infrared Spectroscopy," submitted to *J. Electronic Materials.*

Abstracts Presented in Conferences

1. R. Sudharsanan, S. Perkowitz and A. Rohatgi, "Characterization of Thin $Cd_{1-x}Mn_xTe$ Films by Infrared Spectroscopy," *Bulletin of the American Physical Society*, 33, 716, 1988.

2. Z. C. Feng, S. Perkowitz, A. Erbil, "Characterization of MOCVD-Grown $Cd_{1-x}Mn_xTe$ Films by Photluminescence and Raman Spectroscopy," *Bulletin of the American Physical Society*, 33, 398, 1988.

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GROWTH AND CHARACTERIZATION OF CdMnTe AND CdZnTe POLYCRYSTALLINE THIN FILMS FOR SOLAR CELLS*

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Summary

Thin films of $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ with $x < 0.5$ were deposited by molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) respectively. Electrical and optical properties of these films were studied in addition to the fabrication and characterization of glass/SnO_2/CdS/CdZnTe or CdMnTe/ZnTe/Au front-wall solar cells. Polycrystalline $Cd_{1-x}Mn_xTe$ films with x as high as 0.3 were successfully grown by the MOCVD technique. The $Cd_{0.95}Mn_{0.05}Te$ film gave cell efficiencies in the range 6.0% - 6.7%. Polycrystalline CdZnTe films with band gaps of about 1.65 eV were successfully grown by MBE. The efficiency of CdZnTe was only about 1%, owing to the very high series resistance of the undoped films, although the spectral response of the CdZnTe cell was much better than that of the 6.2% efficient CdMnTe cells. CdZnTe films are now being doped with antimony.

1. Introduction

The 1.5 eV band gap of CdTe film is nearly optimum for high efficiency solar cells. Single-junction polycrystalline thin film heterojunction solar cells have been fabricated from CdTe film on glass/SnO_2/CdS substrates with air mass (AM) 1 cell efficiencies in excess of 10% [1, 2]. Further optimization of film properties could increase the conversion efficiency to about 15%. However, economic calculations suggest that 18% - 20% efficient cells, or modules more than 15% efficient, will be required at a cost of less than

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\$1 W^{-1} to provide electricity at a rate of less than 10¢ kW^{-1} h^{-1}. Such high efficiency polycrystalline cells can only be realized by a tandem cell structure which has optimum band gaps of about 1.7 eV and 1.0 eV for the upper and lower cells respectively. A top cell more than 10% efficient with about 80% subgap transmission coupled with a bottom cell 12% - 15% efficient can produce a tandem cell efficiency in the range 15% - 20%. CdTe does not have the optimum band gap for the top cell; however, a solid solution of CdTe and ZnTe ($E_g \approx 2.2$ eV) or MnTe ($E_g \approx 2.2$ eV) can provide a band gap of about 1.7 eV.

This paper describes the development of polycrystalline CdZnTe and CdMnTe alloys for the top cell. The zinc and manganese contents are varied to tailor the band gap of these films. The electrical and optical properties of these films and the preliminary solar cell results are summarized in this paper.

2. Experimental procedure

2.1. *Thin film growth*

CdMnTe films were grown by metal-organic chemical vapor deposition (MOCVD) on glass/SnO$_2$/CdS substrates in the temperature range 400 - 450 °C. Hydrogen was used as the carrier gas, and dimethyl cadmium, diisopropyl telluride and tricarbonyl manganese were used for the metal-organic sources for cadmium, tellurium and manganese respectively. During typical film growth, the reactor pressure was 250 Torr, the tellurium partial pressure was fixed at 136 mTorr, the manganese partial pressure was 3.5 mTorr, but the cadmium partial pressure was varied in the range 4.6 - 18.5 mTorr to control the band gap, composition and surface morphology. No attempts were made to dope these films intentionally.

Polycrystalline thin films of CdZnTe were grown on glass/SnO$_2$/CdS substrates by molecular beam epitaxy (MBE) in a Varian Gen II machine. High purity (5 N or better) CdTe and ZnTe sources were used for evaporation. In MBE, the substrate temperature affects the surface energy and sticking coefficient of growth components and this influences the physical nature of the film, growth rate and alloy composition. Undoped CdZnTe films were grown with substrate temperatures in the range 100 - 300 °C with a constant ZnTe:CdTe flux ratio of 0.33. From previous experience on single-crystal films, this flux was estimated to give Cd$_{1-x}$Zn$_x$Te films with $x \approx 0.25$. Auger measurements on one polycrystalline film grown at 250 °C confirmed that $x = 0.25$. Some undoped layers were grown at 200 °C with a varying ZnTe:CdTe flux ratio to vary the zinc alloy ratio from 0.09 to 0.50.

2.2. *Cell fabrication*

Front-wall solar cells were fabricated with a glass/SnO$_2$/CdS/CdZnTe or CdMnTe/ZnTe/Au structure. CdS about 1500 Å thick was deposited onto SnO$_2$ coated glass in a pyrolytic reactor from an aerosol containing CdCl$_2$ and thiourea. Polycrystalline CdZnTe or CdMnTe absorber films were deposited onto the glass/SnO$_2$/CdS substrate by MBE or MOCVD. Thin films were annealed at 400 °C for 30 min in N$_2$ followed by a mild etch of Br-methanol before the vacuum evaporation of ZnTe. A copper-doped p$^+$-ZnTe interlayer facilitates the ohmic contact formation when gold contacts are evaporated through a shadow mask with openings of 8 mm^2.

2.3. *Thin film and cell characterization*

Attempts were made to determine the carrier concentration profile and optical property of the films by depth-resolved *C–V* and surface photovoltage (SPV) measurements. Both these measurements are done automatically in an electrochemical etching profiler in which an electrolyte is used to perform precise step-by-step etching coupled with *I–V*, *C–V*, *G–V* and SPV measurements after each step [3, 4]. A Schottky barrier, formed between the electrolyte and the semiconductor, facilitates both *C–V* and SPV measurements. SPV measurements were performed in the wavelength range 0.40 - 0.95 μm. The optics of the SPV set-up have a characteristic response in this wavelength range which results in two bumps in the SPV spectrum at about 560 and 720 nm that are not related to sample quality and should be ignored in the analysis (Fig. 1). The choice of electrolyte is dictated by the properties of the semiconductor. We have found that for these thin films, a solution of 0.2 M NaOH + 0.1 M ethylenediaminetetraacetic acid (EDTA) is an adequate electrolyte for Schottky barrier formation and electrochemical etching.

Some films were grown on glass substrates for transmission measurements using a Cary spectrometer to determine the optical band gap. In

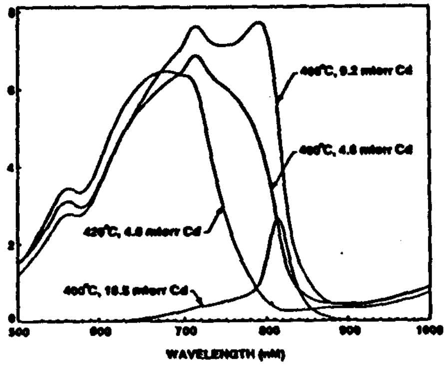


Fig. 1. Surface photovoltage spectra for MOCVD CdMnTe films grown at: (a) 400 °C with a cadmium partial pressure of 4.6 mTorr, 9.2 mTorr, and 18.5 mTorr; (b) 420 °C with a cadmium partial pressure of 4.6 mTorr.

selected instances, Auger measurements were performed to determine and confirm the film composition.

Solar cells were characterized by light and dark $I-V$ measurements and spectral response measurements in the wavelength range 0.35 - 1.1 μm. Cell efficiencies were determined under 100 mW cm^{-2} AM 1 illumination.

3. Results and discussion

3.1. CdMnTe films and solar cells

Table 1 shows the MOCVD conditions used to grow a CdTe film and several CdMnTe films with different manganese contents. Film thicknesses were in the range 0.5 - 2 μm. Figure 1 shows that the manganese content can be increased by reducing the cadmium partial pressure or increasing the growth temperature, since the cut-off edge of the SPV spectra moves toward shorter wavelengths. Figure 2 shows the SPV response of the three films grown on glass/SnO$_2$/CdS substrates, before any heat treatment. CdTe film has the best response in the long wavelength range and a sharp cut-off at 840 nm which corresponds to a band gap of about 1.48 eV. The second film (A093087-1) shows an SPV cut-off at 810 nm or an optical band gap of 1.24/0.810 = 1.53 eV. The third film (A080787-1) showed an SPV cut-off at 740 nm which translates into a band gap of about 1.68 eV. Using the empirical equation [5]

$$x = \frac{E_{CO} - 1.462}{1.435}$$

for the manganese content, valid for $x < 0.3$, we obtain $x = 0.05$ for film A093087-1 and $x = 0.18$ for film A080787-1. E_{CO} is the energy position of the edge for maximum absorption which is assumed to be equal to the cut-off edge at half-maximum of the SPV spectrum. Figure 2 indicates that the film quality or the SPV response of the film with $x = 0.18$ is actually better than that of the film with $x = 0.05$; however, the adhesion of the film with $x = 0.18$ was poor since it lifted off and became very thin during the 400 °C anneal. Therefore, in spite of the near optimum band gap, we were unable to fabricate cells on Cd$_{0.82}$Mn$_{0.18}$Te film. Further work is in progress to improve the adhesion or lower the annealing temperature so the cells can be fabricated on films with high manganese contents.

Figure 3 shows a comparison of the SPV response of Cd$_{0.95}$Mn$_{0.05}$Te film before and after 0.5 μm removal via electrochemical etching. The SPV response of this as-grown film is actually better near the CdS-CdMnTe junction than in the near-surface region. If the film quality were uniform,

TABLE 1

Growth conditions for MOCVD CdMnTe films

Film number	*Material grown*	*Substrate temperature* (°C)	*Time* (min)	P_{Te} (mTorr)	P_{Cd} (mTorr)	P_{Mn} (mTorr)
A080787-1	CdMnTe	420	60	318	4.6	3.5
A093087-1	CdMnTe	420	60	136	9.3	3.5
A110487-1	CdTe	400	120	136	19.9	0
A100187-1	CdMnTe	400	30	126	4.6	4.03
A100187-1	CdMnTe	400	30	126	9.2	4.03
A100187-1	CdMnTe	400	30	126	18.5	4.03

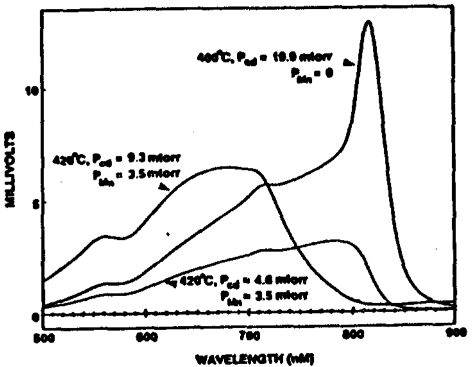


Fig. 2. Surface photovoltage spectra for CdMnTe films grown at: (a) 420 °C with P_{Cd} = 4.6 mTorr; (b) 420 °C with P_{Cd} = 9.3 mTorr; (c) 400 °C with P_{Cd} = 19.9 mTorr and P_{Mn} = 0.

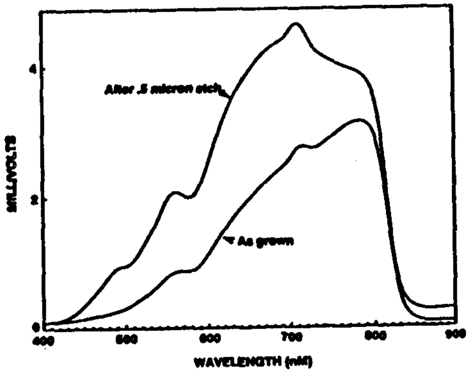


Fig. 3. Surface photovoltage spectra of a Cd$_{0.95}$Mn$_{0.05}$Te film before and after 0.5 μm etching.

the SPV response would have decreased as we approached the CdS-CdMnTe junction because competition develops for the carriers generated between the electrolyte-semiconductor Schottky barrier and the CdS-CdMnTe heterojunction. Figure 3 also indicates that the manganese content is fairly uniform as a function of depth since the SPV cut-off edge remains essentially unchanged. In addition to providing information about the optical band gap and manganese content, the depth-resolved SPV could be used as a quick and powerful tool for studying the uniformity of the films and even process-induced effects, without having to fabricate solar cells.

Figure 4 shows a doping profile in $Cd_{0.95}Mn_{0.05}Te$ film obtained by the depth-resolved $C-V$ measurements in the electrochemical etching profiler. The data give a film thickness of about 0.6 μm and a carrier concentration in excess of 10^{17} cm^{-3} which appears much higher than expected. We are in the process of finding an explanation for any excess charge that may be sensed by $C-V$ measurement on this structure which includes a Schottky barrier on top and a heterojunction underneath.

Solar cells fabricated on film with low manganese content ($x \approx 0.05$) gave cell efficiencies in the range 6.0% - 6.7%, with $V_{OC} = 680$ mV, $J_{SC} = 20.6$ mA cm^{-2}, and a fill factor (FF) of 0.442 - 0.500 (Fig. 5). Dark $I-V$ measurements (Fig. 6) suggest that the low fill factor is due to excess junction leakage current. Attempts are being made to perform deep level transient spectroscopy (DLTS) measurements to investigate traps in the depletion region of the device and to explain the excess leakage current.

Figure 7 shows the spectral response of a 6.2% efficient $Cd_{0.95}Mn_{0.05}Te$ cell when illuminated from the front (CdS) and the back (ZnTe). The data confirm that CdS-CdMnTe is indeed the collecting heterojunction since the front spectral response is much higher. The spectral response cut-off edge (about 810 nm) of the finished cell corresponds very well with the SPV cut-off edge of the as-grown film. This indicates that the manganese content remains unchanged during the cell fabrication.

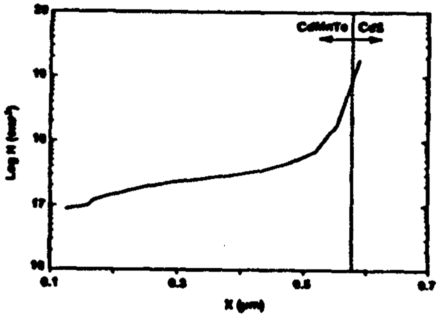
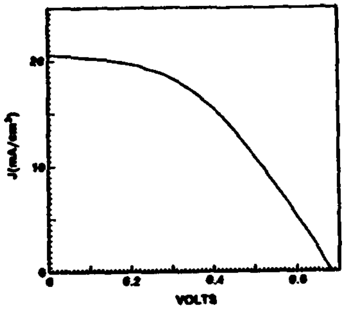


Fig. 4. Doping profile of a $Cd_{0.95}Mn_{0.05}Te$ film obtained by depth-resolved $C-V$ measurements.



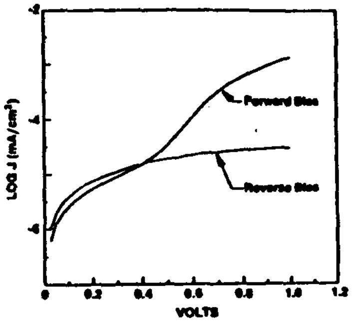


Fig. 5. Illuminated $I-V$ data of a 6.2% efficient polycrystalline CdMnTe cell: $J_{sc} = 20.6$ mA cm^{-2}; $V_{oc} = 680$ mV; FF = 0.442; area, 0.80 cm^2.

Fig. 6. Forward and reverse dark $I-V$ data for a 6.2% efficient CdMnTe cell.

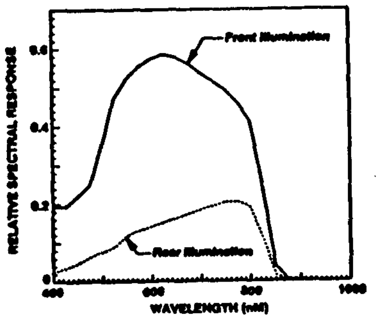


Fig. 7. Spectral response of a 6.2% efficient polycrystalline CdMnTe cell.

3.2. CdZnTe solar cells

Because of the high resistance of the MBE grown undoped CdZnTe films, we have so far been unable to make depth-resolved $C-V$ and SPV measurements. Therefore, we performed the transmission measurements on the films grown on glass slides to determine the optical band gap. Figure 8 shows that the material quality improves with substrate temperature and the sharpest cut-offs are measured on layers grown above 250 °C. Above 300 °C, it becomes somewhat difficult to grow these polycrystalline films and, in addition, the film begins to show more defects in the photomicrographs. Thus 250 °C seems to be an optimum growth temperature for these polycrystalline films. A film grown at 250 °C with a ZnTe:CdTe flux ratio of 0.64 gave an optical band gap of 1.63 eV (760 nm cut-off). The solar cell

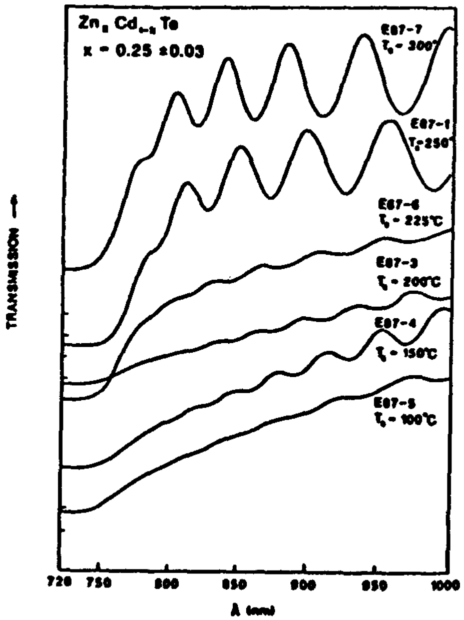


Fig. 8. Transmission data for MBE CdZnTe films grown at different temperatures with a constant ZnTe:CdTe flux ratio of 0.33.

efficiency was only about 1% with V_{OC} = 600 mV, J_{SC} = 4 mA cm^{-2} and FF = 0.28. This low efficiency was primarily caused by the high series resistance (Fig. 9) of the undoped films. In fact, the spectral response (Fig. 10) of the CdZnTe cell was better than the spectral response of the 6.2% efficient CdMnTe cell. We are now in the process of doping these films with antimony during the MBE growth and the cell data on these films will be reported in the near future.

4. Conclusions

CdMnTe and CdZnTe polycrystalline films were successfully grown by the MOCVD and MBE techniques respectively onto glass/SnO$_2$/CdS substrates. The manganese and zinc contents were varied to obtain band gaps in the range 1.60 - 1.75 eV. A depth-resolved SPV technique was successfully applied on CdMnTe films to determine the optical band gap, manganese content, the uniformity and optical properties of the film. Cell efficiencies in the range 6.0% - 6.7% were achieved on Cd$_{0.95}$Mn$_{0.05}$Te film using the glass/SnO$_2$/CdS/CdMnTe/ZnTe/Au front-wall solar cell structure. Solar cells could not be made on films with higher manganese content owing to poor adhesion. Solar cells were fabricated on CdZnTe film with wide band gaps (about 1.65 eV), but cell efficiencies were only about 1% owing to high resistance; however, the spectral response was quite good. Thus, the preliminary work indicates that both Cd$_{1-x}$Zn$_x$Te and Cd$_{1-x}$Mn$_x$Te are promising materials for an optimum band gap top cell. Further work is needed in the area-controlled doping, ohmic contact formation and property optimization before these cells can become a commercial reality.

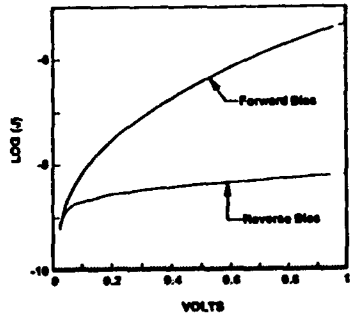


Fig. 9. Dark $I-V$ data for a polycrystalline CdZnTe solar cell: J_{SC} = 4 mA cm^{-2}; V_{OC} = 600 mV; FF = 0.280.

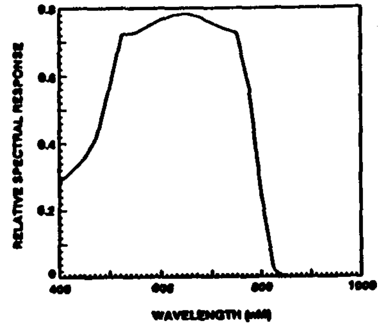


Fig. 10. Spectral response of a polycrystalline CdZnTe solar cell.

Acknowledgment

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WHY THE PHOTOCONDUCTIVITY DECREASES IN a-SiC:H AND a-SiGe:H WHEN THE AMOUNT OF ALLOYING INCREASES*

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Summary

IR, photoconductivity, Raman and photothermal deflection spectroscopy measurements were used to probe the relationship between material quality and the amount of microstructure in glow discharge deposited a-SiC:H and a-SiGe:H films. We find that the microstructure is directly responsible for the decrease in photoconductivity observed in both alloys as a function of increased alloy content. The microstructure does this by causing a decrease in the steepness of the Urbach tail, thus allowing for an increase in both carrier trapping at the wider band edges and carrier recombination at or near the band tails.

1. Introduction

Hydrogenated amorphous silicon based alloys, in particular amorphous silicon carbon (a-SiC:H) and amorphous silicon germanium (a-SiGe:H), are of considerable interest for their integration into a multijunction thin film solar cell [1]. Although considerable success has been achieved in using these alloys in such a device, a major problem remains the decrease in photoconductivity with increased alloying [2, 3]. Recent publications have attempted to link the microstructure to the photoresponse in both alloys [4, 5]. We first review the results of one of these publications [5], where the decrease

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RAMAN SCATTERING CHARACTERIZATION OF HIGH-QUALITY $Cd_{1-x}Mn_xTe$ FILMS GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION

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$Cd_{1-x}Mn_xTe$ films (thickness ~0.5 µm, $x = 0.10 - 0.37$) have been grown by metalorganic chemical vapor deposition on commercial GaAs and glass substrates with and without buffer layers of CdTe and CdS. Raman scattering shows the films to be of high quality, despite the large film-substrate lattice mismatch. CdTe-like and MnTe-like phonon lines are sharp and strong in first and second order with widths $\leq$ 10 cm^{-1}, and clearly appear in combinations up to fourth order. Raman and photoluminescence analysis also establish an optimum growth temperature and limits on the fraction of Mn.

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Much effort has recently been invested in dilute magnetic semiconductors like $Cd_{1-x}Mn_xTe$ (CMT), whose large spin-spin exchange interaction between the localized magnetic moments and the band electrons gives a giant Faraday rotation, a huge spin-flip electronic Raman shift, and other novel magnetic and magneto-optical properties.[1,2] The tunable energy gap, the values of effective mass and lattice constant, and other important parameters also make CMT a promising candidate for electronic and photonic devices like solar cells.[1]

The properties of bulk CMT are well known.[3-6] Thin CMT films and CMT-based superlattices grown by molecular beam epitaxy (MBE) have also been extensively made and studied.[7-11] However, there has been little growth and analysis of low-cost CMT films grown on commercial wafers[12] by other techniques, a necessity for wide use of CMT. This report, the first in a series, shows our progress toward this goal. We have successfully used metalorganic chemical vapor deposition (MOCVD) to grow CMT films (Mn fraction $x = 0.1 - 0.37$) on commercial GaAs and glass wafers. We confirm film quality and optimize growth conditions by Raman scattering, supported by photoluminescence (PL) spectroscopy.

A commercial MOCVD system (Cambridge Instruments MR102) at the Georgia Institute of Technology Microelectronics Research Center was used to grow CMT films with a horizontal reactor. Dimethyl cadmium, di-isopropyl tellurium and tricarbonyl (methylcyclopentadienyl) manganese supplied Cd, Te and Mn, at typical partial pressures of 5, 126 and 4 mtorr respectively. The reactor pressure was 250 torr. Growth rates were typically 0.5 μm/h for substrate temperatures near 420°C. Further details about growth will appear in future publications.

The films, typically 0.5 μm thick, were grown on four different substrate arrangements: a commercial (111) GaAs wafer (CMT/GaAs); a ~2 μm-thick buffer layer of CdTe grown on a (111) GaAs wafer (CMT/CdTe/GaAs); microelectronic glass (CMT/glass); and a wafer composed of ~0.2μm of CdS on ~0.4 μm of SnO_2 on glass (CMT/CdS/SnO_2/glass, or CMT/CSG). In this last wafer, produced commercially by the Boeing Aerospace Corporation, the n^+ CdS layer forms a p-n junction and the SnO_2 layer provides electrical contacting for solar cell use. The CMT/GaAs and CMT/CdTe/GaAs films were deposited on substrates of varied size up to 20 cm^2. The CMT/CSG and CMT/glass films were 1.3 x 1.3 cm (1/2"x1/2") or 1.3 x 2.5 cm (1/2"x1"), adequate for large area solar cells.

X-ray diffraction showed that CMT films grew epitaxially on GaAs and on CdTe/GaAs with a (111) orientation, whereas films on CSG and glass showed randomly oriented polycrystalline structure. Further information came from Raman and PL spectra measured at Emory University. These were excited by the 514 and 488 nm lines from an Ar-ion laser with < 200 mW focused on samples mounted in the near-backscattering geometry and held at ~80K. A scanning double monochromator with a cooled photomultiplier gave simultaneous PL and Raman data, and a triple spectrometer with a cooled optical multichannel analyzer (OMA) gave superior Raman spectra.

We examined about fifty samples by PL and Raman spectroscopy. The sub-set of samples discussed in this paper is described in Table I, where the x values come from our PL data. Figure 1 shows a typical spectrum recorded by the PM system for CMT/CdTe/GaAs sample A0425871 at 80K, displaying a strong, broad PL band with weak Raman features. The position of the PL peak (here, 2.005 eV), which we interpret as the gap energy E_g, gives x according to[4]

$$E_g = 1.585 + 1.51\, x \text{ (eV)} \tag{1}$$

(here, $x = 0.28$). In all cases the full width at half maximum (FWHM) of the peak (here, ~160 meV) far exceeds the expected thermal broadening of ~7 meV and increases with x. The FWHM is a general measure of crystalline perfection, but for a ternary alloy like CMT, it is difficult to untangle compositional, impurity and structural effects. We found also that the FWHM changed only slightly with growth temperatures from 380 to 450°C. In contrast, our Raman spectra exhibited many features sensitive to growth temperature and crystalline perfection, enabling us to characterize film quality and optimize growth conditions.

Figure 2 shows Raman spectra (from the OMA system) for epitaxial CMT/GaAs samples made with different substrate temperatures T_s. CdTe-like and MnTe-like phonon modes are apparent (subscripts 1 and 2, respectively). For T_s = 380°C and 400°C both longitudinal (LO) and transverse (TO) modes appear, although the strong CdTe-like LO_1 mode probably covers the MnTe-like TO_2 mode. For T_s = 420°C and 430°C, only LO_1, LO_2 and their higher order combinations exist. At T_s = 450°C all the sharp CMT lines vanish and new lines appear at 272 and 295 cm^{-1}, near the TO and LO frequencies of the GaAs substrate. When we scanned the Raman beam across this sample, the intensities of these GaAs lines varied down to zero whereas no sharp CMT phonon lines ever appeared, suggesting that films grown at 450°C are nonuniform and of poor quality.

For the remaining temperatures, careful inspection shows that 420°C gives the narrowest Raman lines and the only appearance of third- and fourth-order phonon combinations. Examination of other CMT/CdTe/GaAs and CMT/GaAs samples confirmed that third and fourth order mixtures exist only for films grown at 420°C, which therefore emerges as an optimum substrate temperature for MOCVD growth on GaAs and CdTe/GaAs. Similar analysis shows that this temperature is optimum for CMT/CSG and CMT/glass as well. Another result from this study was that we could not obtain $x > 0.2$ for $T_s < 400°C$.

Figure 3 shows the relation between film quality and substrate, displaying Raman spectra for films grown on each configuration at 420°C, the optimum temperature. CMT/GaAs and CMT/CdTe/GaAs exhibit sharp, strong first and second order CdTe-like and MnTe-like phonon lines with FWHM $\leq$ 10 cm^{-1}. Third and fourth order mode combinations are clear for

CMT/CdTe/GaAs and slightly less so for CMT/GaAs. The CMT film on CdS/SnO_2/glass gives sharp, strong first- and second-order lines only slightly broader than those for CMT/CdTe/GaAs and CMT/GaAs, with weak third-order modes. This again suggests high quality, although somewhat below that for CMT/CdTe/GaAs and CMT/GaAs. The first- and second-order lines from CMT/glass remain strong but are broader than for the other three substrates. No clear third order structures are seen, so that CMT/glass shows the lowest quality of our four sample types.

Our best Raman spectra, for CMT/GaAs and CMT/CdTe/GaAs, are superior to those reported for bulk crystalline CMT, which display only first and second order Raman lines.[5,13] MBE-grown $Cd_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$ superlattices have produced third and fourth order lines, but only under resonant excitation.[2,14] We observe third and fourth order lines at 514.5 nm (2.41 eV) (Fig. 3), and also at 488.0 nm (2.54 eV) and 457.9 nm (2.71 eV) (not shown), far from resonance with our band gap energies of 1.9 - 2.1 eV.

Our observation of Raman modes up to fourth-order in samples not made in MBE-superlattice form and without resonant enhancement is significant evidence, we feel, for the excellent quality of our MOCVD-grown CMT/GaAs and CMT/CdTe/GaAs. Our results show that MOCVD growth of CMT films on different substrates, including inexpensive glass, can be a successful technology. We will continue to grow and analyze these four types of CMT films. As a final comment, we note that the use of varied optical methods is a powerful means to characterize these and other new materials.

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TABLE I. Data for representative set of CMT films grown by MOCVD on varied substrate structures. T_s, substrate temperature during growth; PL peak, energy of main photoluminescence peak, giving the band gap at 80K; x, fraction of Mn as determined from PL peak and Eq. 1.

Sample	Substrate Structure	T_s (^oC)	PL peak (eV)	x
A0203882	GaAs	380	1.75	0.11
A1001872	GaAs	400	1.70	0.10
A0208881	GaAs	420	1.999	0.28
A0203881	GaAs	430	2.008	0.28
A0211881	GaAs	450	2.032	0.30
A0929871	GaAs	420	1.996	0.28
A0425871	CdTe/GaAs	420	2.005	0.28
A0925871	CdTe/GaAs	420	2.146	0.37
A1113871	CdS/SnO_2/glass	420	2.014	0.29
A0216881	glass	420	2.042	0.31

FIGURE CAPTIONS

Figure 1. Combined photoluminescence and Raman results at 80K from a $Cd_{1-x}Mn_xTe$ film grown on a CdTe buffer layer on a (111) GaAs substrate (Sample A0425871, Table I). The large peak is the primary PL feature at the band gap, whereas the small features near 2.50 eV arise from Raman scattering. Spectrum obtained with a scanning double monochromator and photomultiplier detector.

Figure 2. Raman spectra at 80K from $Cd_{1-x}Mn_xTe$ films grown on a (111) GaAs substrate at different substrate temperatures $T_s = 380 - 450^oC$. The x values derived from the PL data are indicated. Spectra obtained with a triple spectrometer and optical multichannel analyzer.

Figure 3. Raman spectra at 80K from $Cd_{1-x}Mn_xTe$ films grown at a substrate temperature of 420^oC on GaAs, CdTe/GaAs, CdS/SnO_2/glass, and glass. TO and LO, transverse and longitudinal optical phonon modes; subscripts 1 and 2, CdTe-like and MnTe-like modes. Note appearance of second, third and fourth order mode combinations. Spectra obtained with a triple spectrometer and optical multichannel analyzer.

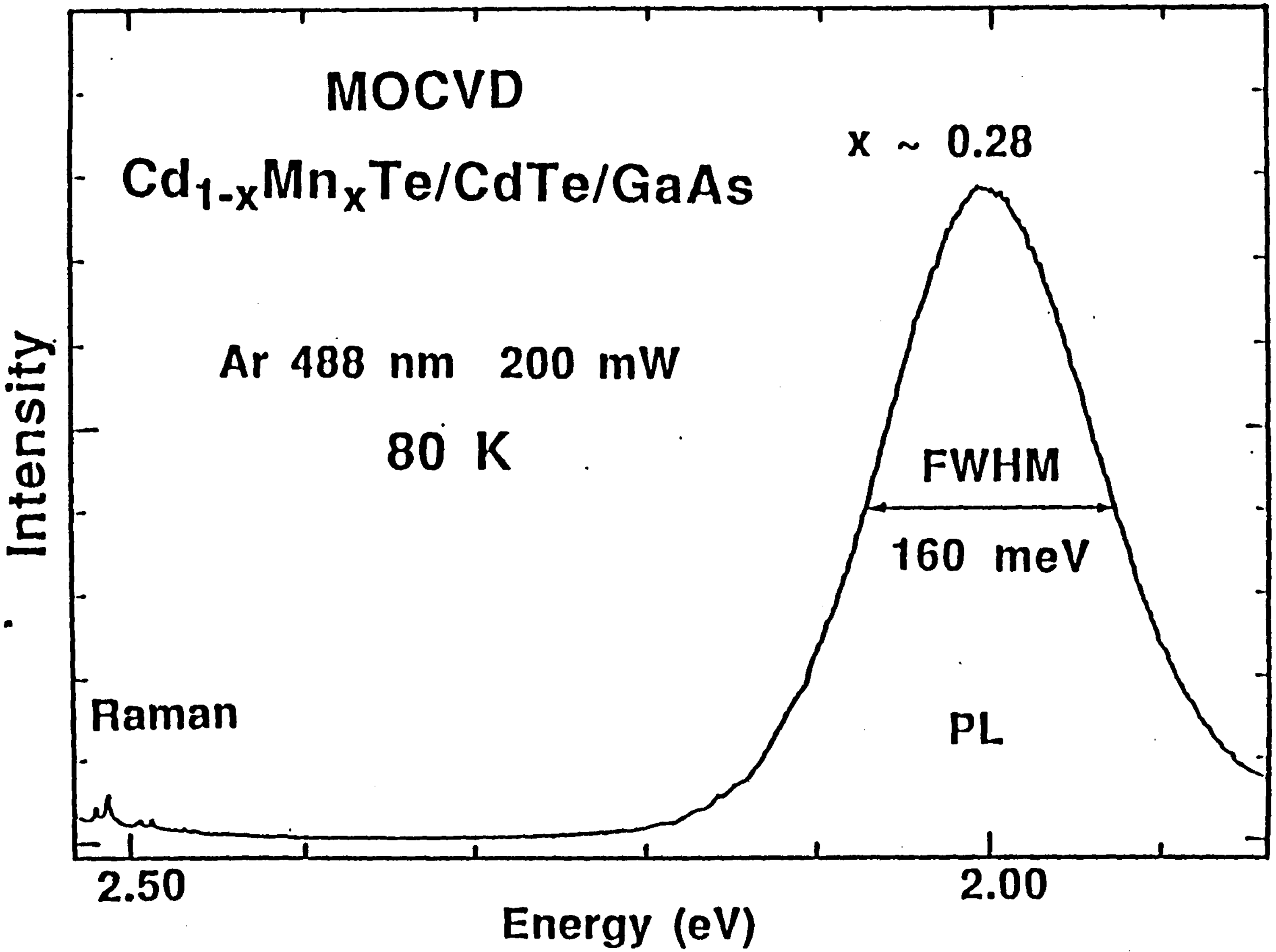
MOCVD
Cd1-xMnxTe/CdTe/GaAs
x ~ 0.28
Ar 488 nm 200 mW
80 K
FWHM
160 meV
Raman
PL
Intensity
2.50
2.00
Energy (eV)

Fig. 1

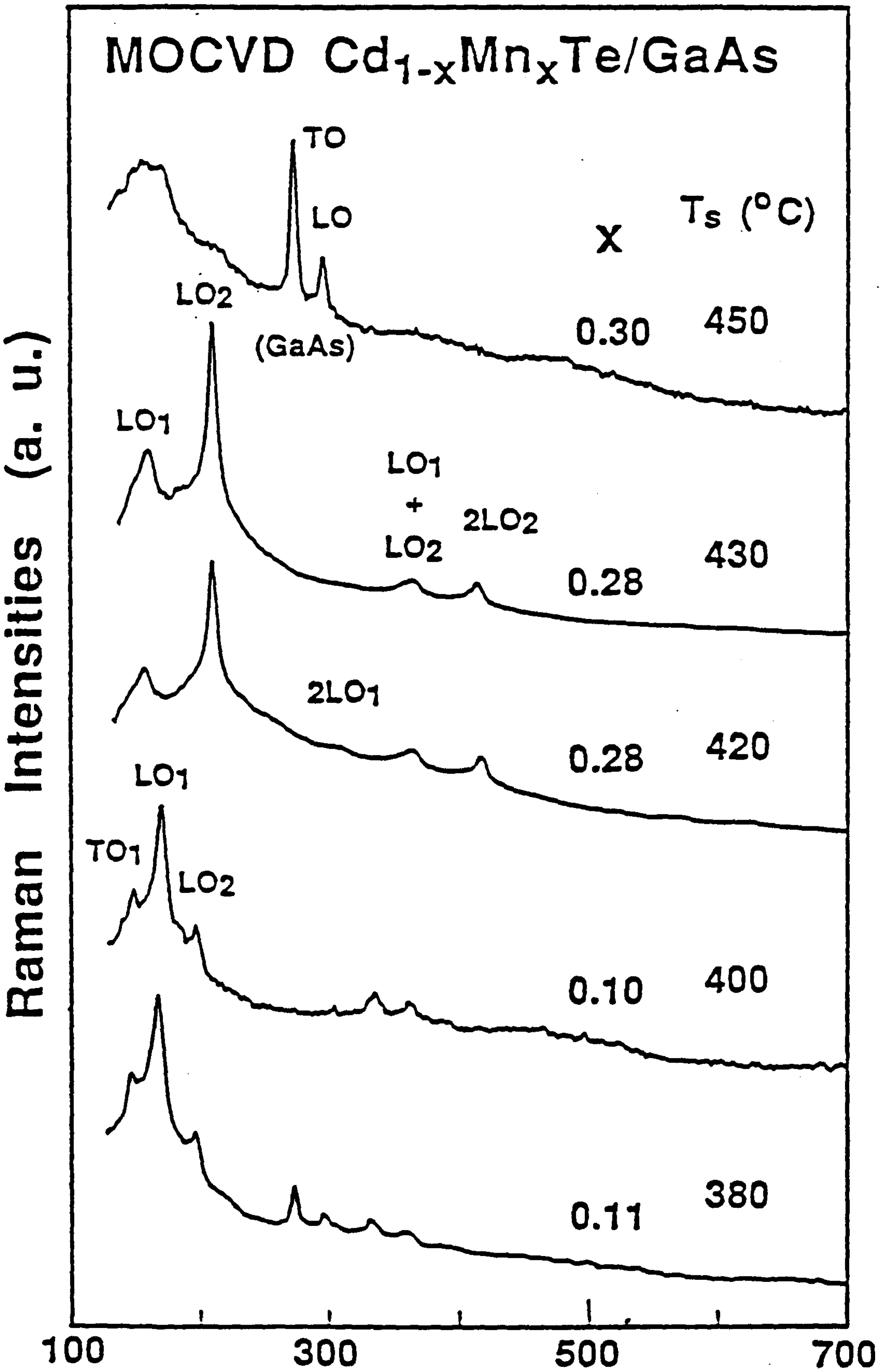
MOCVD $Cd_{1-x}Mn_xTe$/GaAs
TO
LO
(GaAs)
X
T_s (°C)
0.30
450
LO2
LO1
LO1
+
LO2
2LO2
0.28
430
2LO1
0.28
420
LO1
TO1
LO2
0.10
400
0.11
380
Raman Intensities (a. u.)
100
300
500
700
Raman Shift (cm-1)

Fig. 2

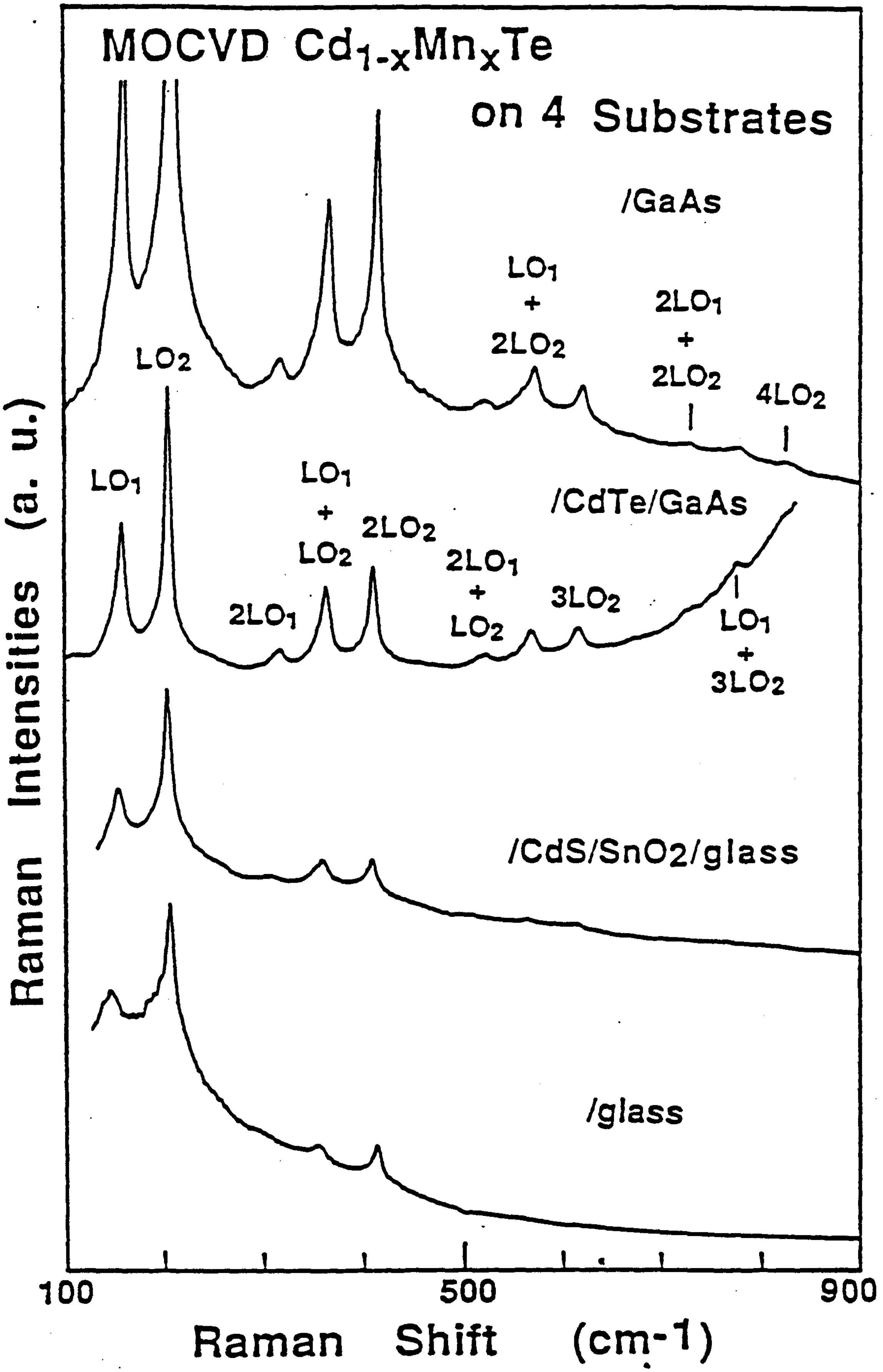
MOCVD $Cd_{1-x}Mn_xTe$
on 4 Substrates
/GaAs
LO_2
LO_1 + $2LO_2$
$2LO_1$ + $2LO_2$
$4LO_2$
LO_1
/CdTe/GaAs
LO_1 + LO_2
$2LO_2$
$2LO_1$
$2LO_1$ + LO_2
$3LO_2$
LO_1 + $3LO_2$
/CdS/SnO2/glass
/glass
Raman Intensities (a. u.)
100
500
900
Raman Shift (cm-1)

Fig. 3

WIDE BANDGAP THIN FILM SOLAR CELLS FROM CdTe ALLOYS

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ABSTRACT

Ternary films of CdZnTe and CdMnTe were grown by molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), respectively, on glass/SnO_2/CdS substrates with target bandgap of 1.7 to 1.8 eV for solar cell applications. X-ray diffraction, surface photovoltage spectroscopy, and Auger electron spectroscopy measurements were performed to estimate bandgap, compositional uniformity, and interface quality of the films. Front-wall CdTe cell (glass/SnO_2/CdS/CdTe/ZnTe/Metal) efficiencies were ~9%, while CdZnTe and CdMnTe efficiencies were ~3.6% and 6%, respectively. n-i-p cell efficiencies were consistently higher than n-p cells. Optimum cell processing temperature for CdZnTe films was found to be less than 400°C. Higher processing temperatures caused a shift in bandgap coupled with film quality degradation.

INTRODUCTION

The 1.45 eV bandgap of CdTe films is nearly optimum for a single junction high efficiency solar cell. Polycrystalline thin film heterojunction solar cells have been fabricated from CdTe films on glass/SnO_2/CdS substrates with AM1 cell efficiencies in excess of 10% [1,2]. Further optimization of film properties could increase conversion efficiencies to about 15%. However, economic calculations suggest that 18-20% efficient cells, or greater than 15% modules, will be required at a cost of less than $1/Watt to provide electricity at a rate of less than 10¢/kWhr. Such high efficiency polycrystalline cells can only be realized by a tandem cell structure which has optimum bandgap of ~1.7 eV and 1.0 eV for the upper and lower cells, respectively. A greater than 10% efficient top cell with about 80% subgap transmission coupled with a 12-15% efficient bottom cell can produce a tandem cell efficiency in the range of 15-20% [3]. CdTe does not have the optimum bandgap for the top cell, however, an alloy of CdTe and ZnTe (E_g ~2.2 eV) or MnTe (E_g ~2.2 eV) can provide a bandgap of ~1.7 eV. So far, only few attempts have been made to determine the feasibility of these materials for solar cell applications.

In this paper, we report the preliminary results of our investigation on growth, characterization, and cell fabrication on CdTe, CdZnTe, and CdMnTe films which resulted in efficiencies of 7-9%, 3.6%, and 6%, respectively.

EXPERIMENTAL PROCEDURE

Film Growth

CdZnTe and CdTe films were grown by molecular beam epitaxy (MBE) using a Varian Gen II MBE system. Elemental sources were used for all constituents having a purity of at least 5N. The films were grown on glass/SnO_2/CdS substrates. The substrates were baked out at 250°C for 3-4 hours before film growth. The substrate temperature was kept at 275°C for 30 minutes to commence film growth and increased to 300°C for the remainder of the run. Growth rates were typically ~1 μm/hr for both CdTe and CdZnTe. Film purity was monitored using in-situ Auger measurements which detected the presence of Cd, Te, and Zn only, indicating high purity of the as-grown MBE films.

CdTe and CdMnTe films were grown by metalorganic chemical vapor deposition (MOCVD) on glass/SnO_2/CdS substrates. CdMnTe films were grown using dimethylcadmium, diethyltellurium, and tricarbonyl methylcyclopentadienyl manganese as source materials for Cd, Te, and Mn, respectively. The CdMnTe films were grown at substrate temperature 420°C, while CdTe films were grown at substrate temperature in the range of 300° to 400°C with diallyltellurium as a source for Te.

Film Characterization

X-ray diffraction (XRD) measurements were performed on these films to determine both the film composition and the possible formation of mixed phases. The lattice constant was found by extrapolation method [4]. Surface photovoltage (SPV) measurements were performed using an electrochemical etching profiler which has an advantage over techniques, such as optical absorption in that measurements can be made in a depth-resolved fashion so that compositional uniformity and material quality can be determined by tracking variations in the absorption edge and the magnitude of the SPV response, respectively [5]. The SPV measurements were made using an electrolytic solution consisting of 0.2 M NaOH+0.1 M EDTA (ethylendiamminetetraacetic acid) which forms a Schottky barrier contact on these films. To study the compositional uniformity in more detail, Auger electron spectroscopy (AES) was performed on CdTe and CdZnTe films using a Physical Electronics Model 600 Scanning Auger Multiprobe. The angle between the sample normal and the electron beam was 45°.

Cell Fabrication

Front-wall solar cells were fabricated with a glass/SnO_2/CdS/CdZnTe or CdMnTe/ZnTe/Ni structure. In selected instances, MBE and MOCVD CdTe solar cells were made with identical structures. The films were annealed at 400°C for 30 minutes in breathing air followed by a mild etch of Bromine methanol before the vacuum evaporation of a Cu-doped p^+-ZnTe interlayer which facilitates the ohmic contact to subsequently evaporated 8 mm^2 Ni dots.

RESULTS AND DISCUSSIONS

Bandgap, compositional uniformity, and interface quality were determined by a combination of XRD, SPV, and AES techniques. Figure 1 shows XRD of MBE-grown polycrystalline CdTe and CdZnTe films grown on CdS/SnO_2/glass substrates, which gave 7.5% and 3.6% efficiencies. The lattice constant "a" of the CdZnTe film determined by an extrapolation method [4] was used to estimate the Zn content (x) in CdZnTe as-grown films according to a(x)=6.481-0.381X Å. The estimated atomic concentration (x) of Zn in CdZnTe film was 0.40. The bandgap of this film was found to be ~1.7 eV from the relationship between x and bandgap (E_g) derived from optical absorption measurements [6]. Same procedure was used to determine bandgap of CdMnTe films from X-ray measurements [7]. X-ray plots in Fig. 1 clearly indicate that there are no other mixed phases present in the CdZnTe film since only peaks corresponding to cubic CdZnTe are observed.

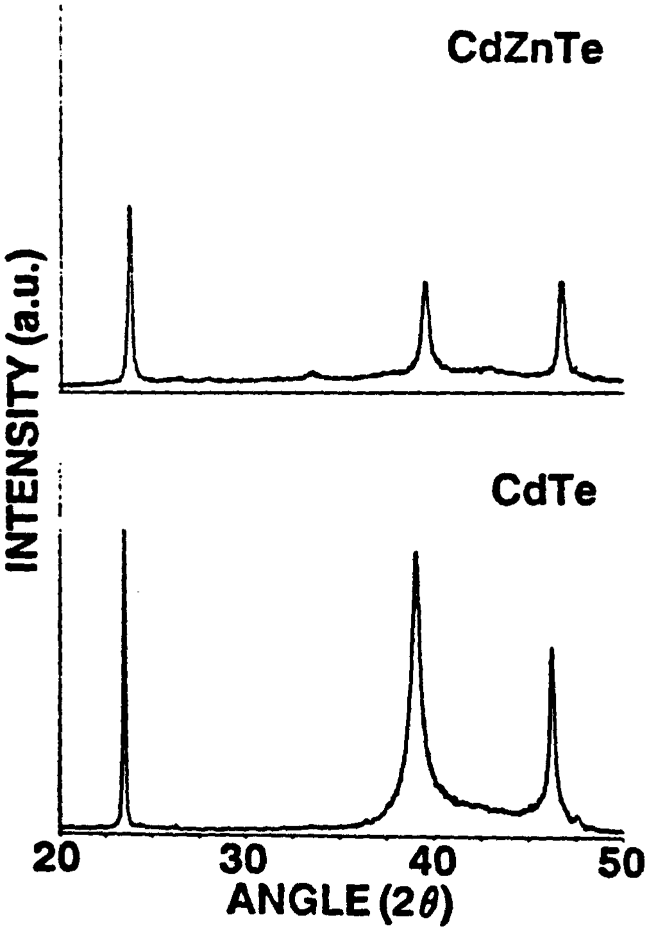

Fig. 1 X-Ray Diffractogram of MBE-Grown CdTe, and CdZnTe Polycrystalline Films Grown on Glass/SnO_2/CdS Substrates.

Figure 2 shows the SPV spectra of the same MBE-grown CdTe and CdZnTe films along with MOCVD-grown CdTe and CdMnTe polycrystalline films. The bandgaps found from the midpoint of the absorption edge were 1.45 eV (MBE-CdTe), 1.7 eV (CnZnTe), 1.45 eV (MOCVD-CdTe), and 1.7 eV (CdMnTe), in good agreement with X-ray measurements. Notice that the cutoff edges of MBE-grown CdTe films are much sharper than the CdMnTe bandedge. The broad shape of the CdMnTe SPV spectrum suggests nonuniformly distributed Mn within the film.

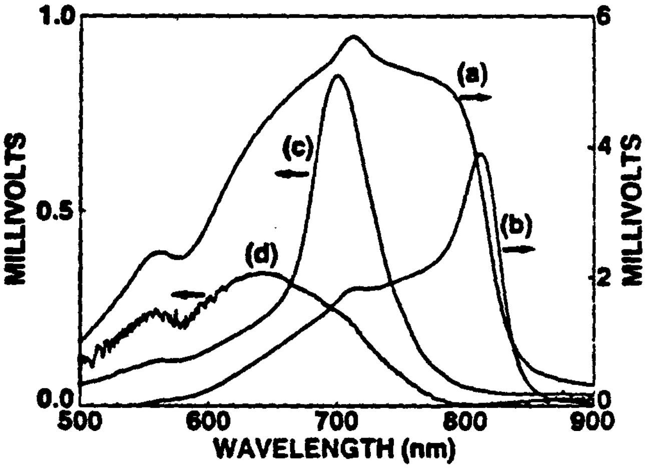

Fig. 2 Surface Photovoltage Spectra of (a) MBD-CdTe, (b) MOCVD-CdTe, (c) MBE-CdZnTe, and (d) MOCVD-CdMnTe Polycrystalline Films Grown on Glass/SnO_2/CdS Substrates.

In order to get a more direct indication of depth resolved composition as well as interface quality, AES measurements were performed on these films. Figure 3 shows the Auger depth profile analysis of MBE-grown CdTe and MOCVD-grown CdMnTe polycrystalline films which gave 7.5% and <1% efficiencies, respectively. The Cd and Te lines in CdTe films grown by MBE and MOCVD, and the Cd, Te, and Zn lines in MBE-CdZnTe were flat indicating uniform composition. In addition, the film interface with CdS was found to be sharp (Fig. 3). However, in the case of CdMnTe film, the Cd, Te, and Mn lines were not flat, confirming compositional

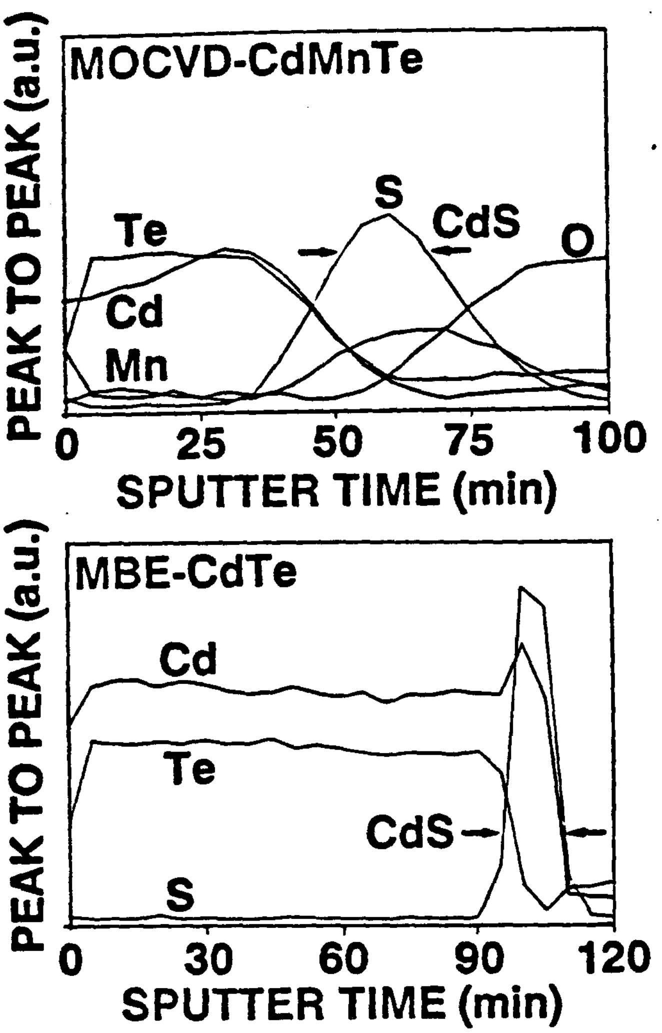

Fig. 3 Auger Depth Profile Plots of MBE-CdTe and MOCVD-CdMnTe Polycrystalline Films on Glass/SnO_2/CdS Substrates.

nonuniformity as suggested by the SPV results. Furthermore, the CdMnTe and CdS interface was broad and showed Mn accumulation due to interdiffusion, probably resulting from relatively high temperature (420°C) used in the growth of the CdMnTe film.

CELL CHARACTERIZATION AND ANALYSIS

Both n-p and n-i-p CdTe and CdZnTe solar cells were fabricated. For n-i-p cells, a p^+-ZnTe film was deposited on top of the absorber layer prior to back contact metallization. Figure 4 shows the spectral response of n-p and n-i-p CdTe and CdZnTe solar cells. The n-i-p spectral response was higher over most of the spectral range in both cases. This is consistent with higher values of J_{sc}, V_{oc}, fill factor, and efficiency of n-i-p cells. Table 1 gives the solar cell parameters of CdTe, CdZnTe, and CdMnTe solar cells.

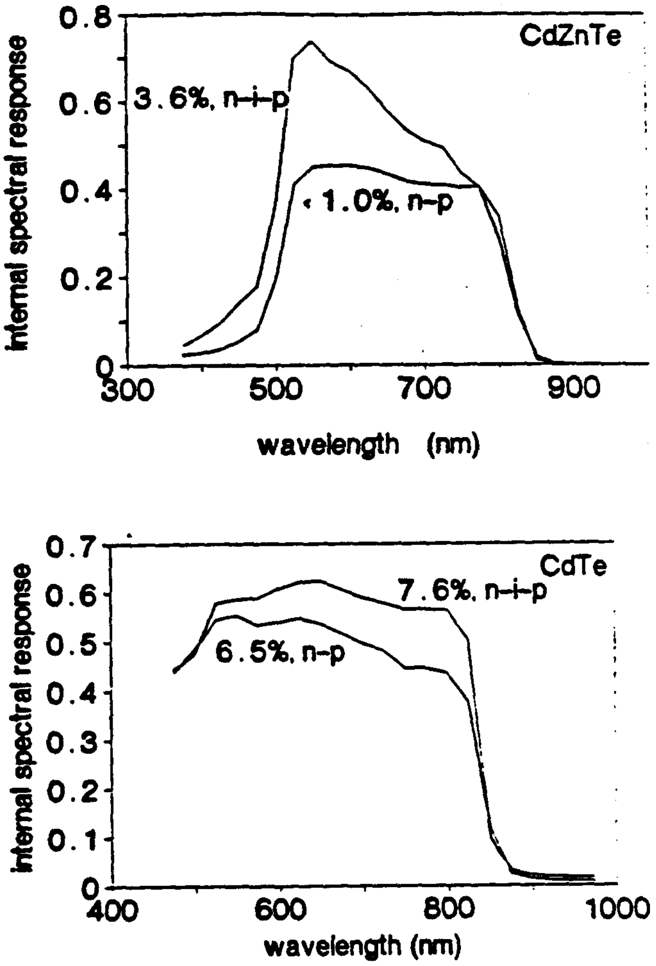

Fig. 4 Spectral Response of n-p and n-i-p CdTe and CdZnTe Cells

Table 1. Solar Cell Parameters of Our Best CdTe, CdZnTe, and CdMnTe n-i-p Cells. The Zn Concentration is 40% in CdZnTe and Mn Concentration is 10% in CdMnTe Films.

Samples	Efficiency %	V_{oc} mV	J_{sc} mA/cm^2	Fill Factor
MBE-CdTe	7.1	740	17.1	55.7
MBE-CdTe	7.6	666	17.5	65.3
MOCVD-CdTe	9.3	713	22.6	57.7
MBE-CdZnTe	3.6	511	14.4	48.4
MOCVD-CdMnTe	6.0	680	20.6	44.2

The cell data and spectral response measurements indicate that we were successful in making 7.5-9.3% polycrystalline CdTe solar cells by MBE and MOCVD techniques with V_{oc} as high as 740 mV and J_{sc} approaching 17.4 mA/cm^2. Fill factor was somewhat low because of high series resistance.

We were successful in tailoring the bandgap of as-grown CdZnTe and CdMnTe to the target value of 1.7-1.8 eV. However, as discussed later, the cell processing resulted in bandgap reduction of CdZnTe films, whereas no appreciable bandgap reduction was observed in CdMnTe film. CdZnTe cell efficiencies were around 3.6% with V_{oc} 511 mV and J_{sc} 14.4 mA/cm^2 which, to the best of our knowledge, is the highest efficiency of CdZnTe/CdS solar cell to-date but not high enough to produce 18-20% efficient polycrystalline tandem cells. CdMnTe efficiencies with low Mn content (<10%) and E_g=1.53 eV were around 6%. Detailed information about 6% CdMnTe has been published elsewhere [8]. So far, attempts to fabricate CdMnTe cells with higher Mn content (>15%) have resulted in cell efficiencies of less than 2%. Work is in progress to optimize the film growth and processing temperature to achieve high efficiency cells. Attempts are being made to understand the material properties, its control, end response to heat treatment in order to fabricate higher efficiency cells.

The spectral response, Fig. 4, of the CdZnTe films indicate that E_g was reduced from 1.7 eV prior to processing to 1.55 eV after processing. In order to understand the decrease in bandgap, transmission measurements were performed on these films before and after processing. Figure 5 shows the transmission data for these films. The spectra of the as-grown films indicate that CdZnTe films have higher subbandgap transmission (lower subbandgap absorption) than CdTe. This difference is not necessarily due to defects but most likely is related to difference in absorption coefficient or bandgap. After annealing at 410°C for 30 minutes (optimum condition for CdTe), CdZnTe films showed a decrease in bandgap, Fig. 5b, which is consistent with the spectral response measurements taken on these cells. One of the CdZnTe films was annealed intentionally for a longer time (50 minutes) and the transmission of this film showed not only a decrease in bandgap but also a significant increase in subbandgap absorption which is indicative of process induced defects that may be related to loss of Zn from its substitutional sites in the film as suggested by reduced bandgap. Auger depth profile analysis on this film after processing indicated a nonuniform distribution of Te throughout the film with some Zn segregation to the ZnTe/CdZnTe interface within the bulk film, however, Zn line leveled off close to the value found before processing. This possibly indicates that Zn has left its lattice sites in CdZnTe and may be forming other defect complexes which can result in the observed increase in subbandgap absorption. This hypothesis was supported by the very low cell efficiency (0.6%) observed for this particular film. The above results suggest that processing time and temperature used for CdZnTe solar cells were not optimum.

In an attempt to optimize cell processing temperature, SPV measurements were performed on CdZnTe films annealed at different temperatures. Figure 6 shows the SPV spectra of CdZnTe film annealed in air for 30 minutes in the temperature range 360° to 410°C. The SPV response increases

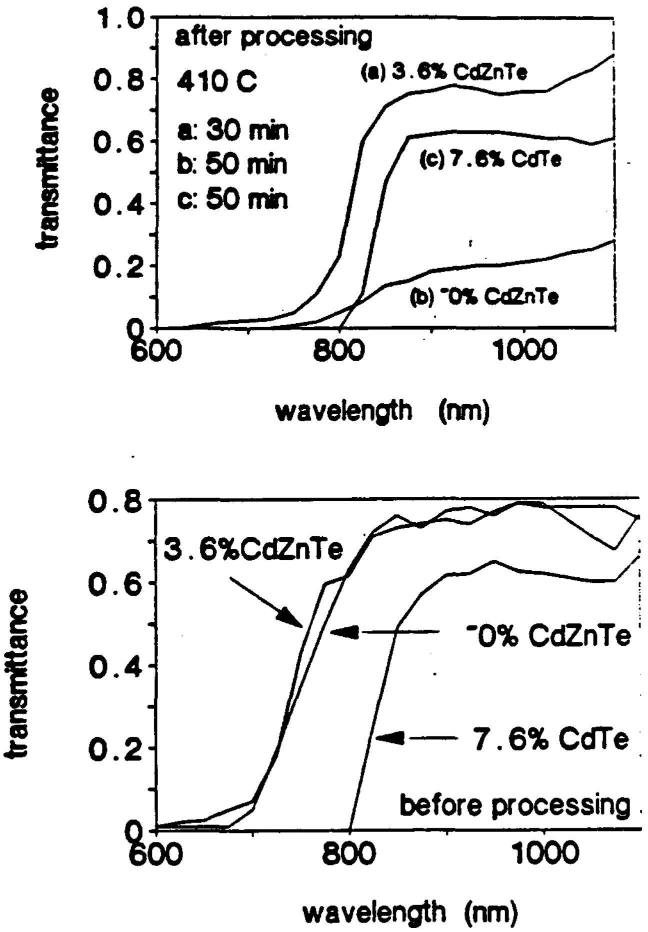

Fig. 5 Transmission Spectra of CdTe and CdZnTe Films Before and After Processing.

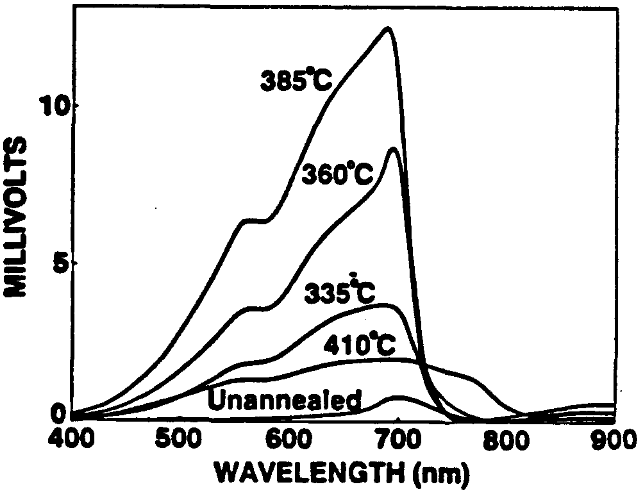

Fig. 6 Surface Photovoltage Spectra of CdZnTe Film Annealed at Different Temperatures in Air for 30 Minutes.

without any change in the bandgap or Zn content up to an annealing temperature of 385°C. This indicates that annealing improves the film quality. However, SPV response of the film annealed at 410°C decreased drastically. This quality degradation was associated with a shift in the absorption edge towards low bandgap, identical to what was observed in the transmission measurements in Fig. 5. These results suggest that the optimum annealing condition for MBE-grown CdZnTe film is 385°C. The 3.7% CdZnTe solar cell went through the 410°C/30 min. anneal, which may be the reason for low efficiency. Cells are now being fabricated with optimum annealing condition with the goal of achieving CdZnTe efficiencies approaching 10%.

CONCLUSIONS

Both MBE and MOCVD growth techniques have been used to fabricate CdTe based solar cells. Without any material growth and design optimization, CdTe front-wall cells (glass/SnO_2/CdS/CdTe/ZnTe/Metal) with efficiencies in the range 7-9% were fabricated. Thickness optimization is being done to improve the CdTe cell efficiencies beyond 10%. MBE CdZnTe and MOCVD CdMnTe films with bandgap around 1.7-1.8 eV have been deposited on glass/SnO_2/CdS substrates. Unlike the CdTe cells, the optimum process/annealing temperature for ternary cells was found to be lower than 400°C. MBE films showed uniform composition and sharp interfaces but MOCVD CdMnTe films grown at 420°C showed broad interface and compositional nonuniformity. Best n-i-p CdZnTe cell efficiencies were ~3.6% and CdMnTe (<10% Mn) cell efficiencies were ~6%. Although these are some of the highest efficiencies reported to-date on CdTe based alloys, further improvements are necessary to make respectable absorber films for the top cell in the tandem cell design.

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Characterization of MOCVD-Grown CdMnTe Films
by Infrared Spectroscopy

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Single crystal $Cd_{1-x}Mn_xTe$ (x = 0.10 - 0.30) films have been grown by metalorganic vapor deposition (MOCVD) on (111) GaAs substrates with and without CdTe buffer layers, at substrate temperatures of 380° to 450°C. Infrared phonon spectra reveal that the optimum substrate temperature for good film quality with reasonable Mn concentration is about 420°C in agreement with Raman measurements. Spectral analysis also gives values for Mn concentration that agrees with photoluminescence measurements, and determines film thickness.

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Dilute semimagnetic semiconductors have interesting fundamental properties like large Faraday rotation and giant negative magnetoresistance [1]. One of these materials, $Cd_{1-x}Mn_xTe$ has been studied in bulk and thin film form [2-4] and has been used in quantum wells and superlattices grown by molecular beam epitaxy [3,4]. $Cd_{1-x}Mn_xTe$ is potentially useful as an absorber to increase the efficiency of tandem solar cells [5]. We have used metalorganic chemical vapor deposition (MOCVD) to grow single crystal and polycrystalline $Cd_{1-x}Mn_xTe$ films for $Cd_{1-x}Mn_xTe/CdS/SnO_2$/glass solar cells. In preliminary work, Nouhi and Stirn [6] have reported MOCVD growth of single crystal $Cd_{1-x}Mn_xTe$ films on GaAs (100), but the optimum growth conditions and kinetics are not well understood. In this letter, we show the optimization of growth temperature of single crystal $Cd_{1-x}Mn_xTe$ on GaAs (111) substrates from infrared (IR) data and derive values for x and film thickness.

The MOCVD growth was performed at the Georgia Institute of Technology with a commercial system (Cambridge Instruments MR102). The growth details are given elsewhere [7]. The crystallinity of the films was determined from X-ray diffraction measurements. Thin films grown on GaAs (111) and CdTe/GaAs (111) substrates were found to be (111) single crystals, while films deposited on CdS/SnO_2/glass were polycrystalline with no preferred orientation.

Infrared reflection measurements were made over 10-240 cm^{-1}, using a Fourier spectrometer with a Golay cell detector. The spectra were recorded with a resolution of 2 cm^{-1} at room temperature.

Figure 1 shows the infrared spectra of single crystal CdMnTe/CdTe/GaAs films, grown at different substrate temperatures. The peaks at 140 and 180 cm^{-1} correspond to the CdTe-like and MnTe-like transverse optical (TO) phonon modes at room temperature [8-10]. Although the TO frequencies hardly vary with Mn concentration, the remaining phonon parameters - strength, damping constant, and high frequency dielectric constant - do [10]. This allows the determination of Mn concentration in these films.

At substrate temperature T_s = 380°C, the spectrum has a strong CdTe-like peak (140 cm^{-1}) and a very weak MnTe-like peak (180 cm^{-1}). As T_s increases to 420°C, the strength of the MnTe-like mode increases with a corresponding decrease in the strength of the CdTe-like mode. This suggests a higher Mn concentration, perhaps occurring as T_s approaches the $TCPM_n$ compound cracking temperature at 450°C. At T_s = 450°C, the MnTe-like mode is like that at 420°C, but the CdTe-like mode is weaker. This indicates that Mn incorporation remains high but the film seems to become nonstochiometric. This reduction in quality may occur due to disassociation of CdTe, leaving excess Cd or excess Te in the film. Below 420°C, the film quality is good but the Mn incorporation is less than 5%. Hence, the optimum substrate temperature for growing good quality single crystal $Cd_{1-x}Mn_xTe$ films on GaAs with reasonable Mn concentration ($x > .10$) is 420°C. Photoluminescence (PL) and Raman measurements also support these findings [8]. Raman spectra of the films grown at 420°C show sharp high-order phonon peaks, whereas at 450°C, the high-order phonon peaks disappear, indicating poor film quality.

To estimate the Mn concentration and film thickness, the reflectivity spectra were analyzed using a simple model for the phonons. (We consider only phonons because the reflectivity seems to have no free carrier contribution.) The dielectric function is represented by a Lorentzian oscillator for each phonon:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_{j=1}^{2} S_j \omega^2_{TO_j} / (\omega^2_{TO_j} - \omega^2 - i\Gamma_j \omega)$$

where ω_{TO_j}, S_j, Γ_j, and ε_∞ correspond to resonance frequency, strength, damping constant, high frequency dielectric constant, and j = 1,2 correspond to CdTe and MnTe, respectively. Using the known phonon parameters versus x [10] and standard expressions for reflectivity which include thickness of the films, we fitted the reflectivity data. We varied x, film thickness, and buffer layer thickness and the results are shown in Figure 2 for one particular film. We obtained x = 0.25 ± 0.05, close to the value of 0.28 from PL [7]. We found a film thickness of 0.75 μm, near the value 0.7 μm estimated from the CdMnTe growth rate. Our fitted value of buffer layer thickness also agrees with the result from the growth rate.

Table 1 gives the results of similar analyses for four CdMnTe films grown at 420°C, showing that the x values and film thicknesses are in reasonable agreement with other determinations. PL measurements at different points on the surface of sample A0925871 gave x values from 0.18 to 0.35. The infrared beam tends to average over such variation, because it covers a larger area and penetrates further into the film than does the visible light PL beam. This explains why the infrared value for x agrees so well with the mean of the PL values.

Our results show the power of infrared spectroscopy to return varied characterization information which would normally require separate measurements. The determination of an optimum MOCVD growth temperature (420°C) for CdMnTe, the accurate measurement of x values, and the measurement of film thickness would otherwise involve a combination of Raman and PL spectroscopy and growth information. The infrared analysis has contributed to our successful growth of single crystal CdMnTe films on CdTe/GaAs and GaAs substrates, and can be effectively applied to other thin film compound semiconductors.

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TABLE I

Values of Mn concentration x and film thickness derived from the analysis of infrared spectra of single crystal $Cd_{1-x}Mn_xTe/CdTe/GaAs$ (111) films and x values from PL measurements

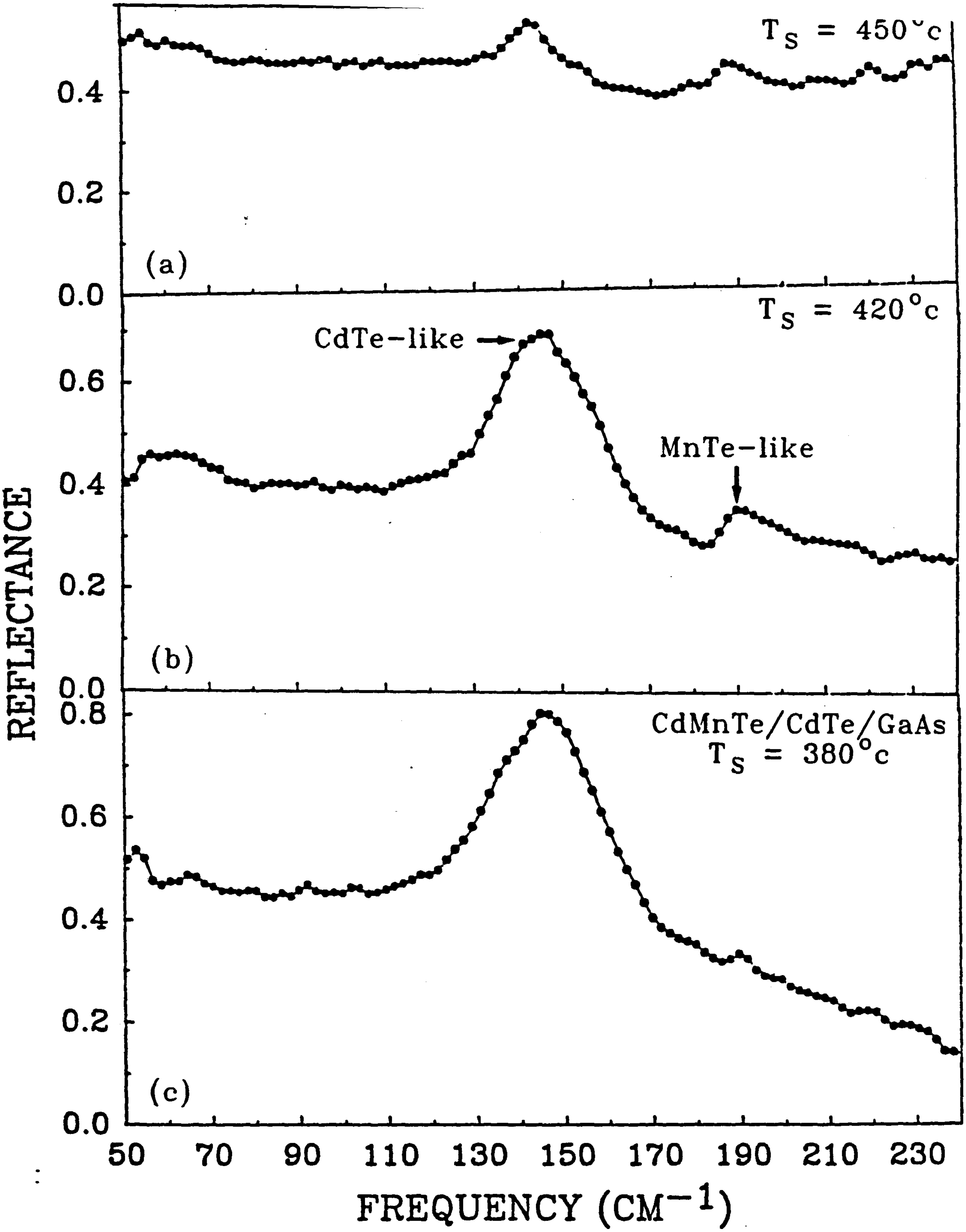
	Infrared		PL
Sample #	X	Thickness μm	X
A0425871	0.25	0.60	0.28
A0623872	0.15	1.50	0.11
A0918871	0.05	0.70	0.06
A0925871	0.25	0.70	0.26+

+ PL measurements indicated a variation in the Mn concentration (0.18-0.35). The mean value is quoted.

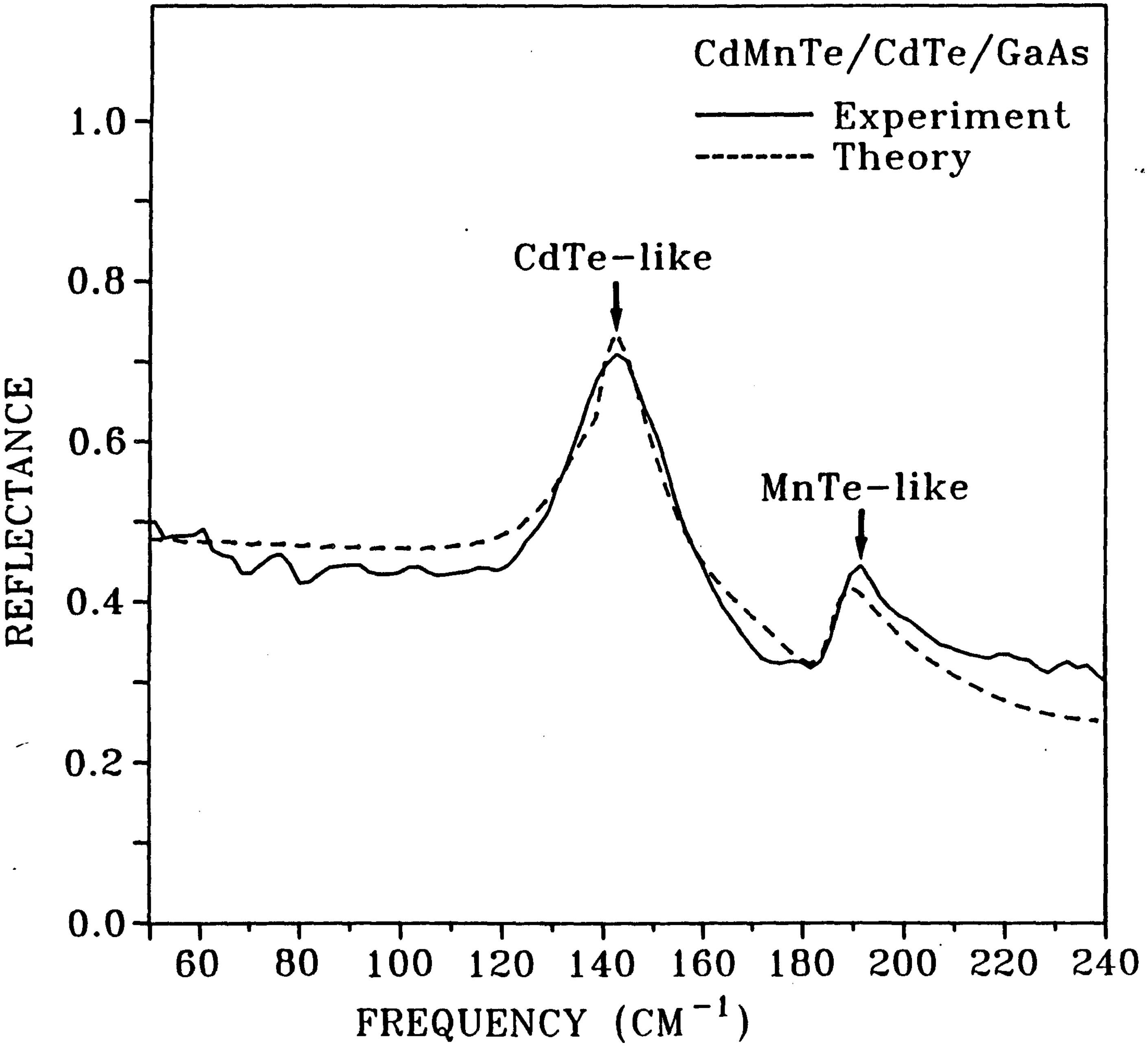
FIGURE CAPTIONS

Figure 1. Infrared reflectivity spectra at 300 K of $Cd_{1-x}Mn_xTe$/CdTe/GaAs single crystal films grown at different substrate temperatures; a. 450°C, b. 420°C, c. 380°C.

Figure 2. Measured (solid line), and calculated (dashed-line) reflectivity spectra of single crystal $Cd_{0.75}Mn_{0.25}Te$ film grown on CdTe/GaAs substrate.



T_S = 450°c
(a)
T_S = 420°c
CdTe-like
MnTe-like
(b)
CdMnTe/CdTe/GaAs
T_S = 380°c
(c)
REFLECTANCE
0.0
0.2
0.4
0.6
0.8
50
70
90
110
130
150
170
190
210
230
FREQUENCY (CM^{-1})


CdMnTe/CdTe/GaAs
Experiment
Theory
CdTe-like
MnTe-like
REFLECTANCE
0.0
0.2
0.4
0.6
0.8
1.0
60
80
100
120
140
160
180
200
220
240
FREQUENCY (CM^{-1})

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16. Abstract (Limit: 200 words)

This report contains results of research on high-efficiency cadmium and zinc telluride based thin-film solar cells from June 1987 to May 1988. CdTe and CdZnTe and CdTe and CdMnTe films were grown on CdS/SnO_2/glass substrates by molecular beam epitaxy and metal-organic chemical vapor deposition, respectively. As-grown films were characterized by x-ray diffraction, surface photovoltage spectroscopy, and infrared, Raman, and Auger electron spectroscopy, among others, for composition, bulk uniformity, thickness, and film and interface quality. Single-crystal films were grown simultaneously to understand the growth conditions of the polycrystalline films. Cell efficiencies ranging from 6.0% to 6.7% were achieved with the $Cd_{0.95}Mn_{0.05}Te$ film employing the glass/SnO_2/CdS/CdMnTe/ZnTe/Au front-wall solar cell structure. Cells fabricated by using CdZnTe films yielded efficiencies from 3.0% to 3.6%.

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