High-Efficiency, Thin-Film Cadmium Telluride Photovoltaic Cells

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SUMMARY

This project at the University of Toledo seeks to develop and optimize the process of radio-frequency (rf) sputtering for the fabrication of thin-film solar cells on glass. Our emphasis is on CdTe-related materials including CdTe, CdS, ZnTe, and ternary alloy semiconductors. Pulsed laser physical vapor deposition (LPVD) is also used for exploratory work on these materials especially where alloying or doping are involved and for the deposition of cadmium chloride layers. For the sputtering work we have implemented, over the past year, a two-gun sputtering chamber with optical access for temperature monitoring and growth rate monitoring. We have studied the optical and electrical properties of the plasmas produced by two different kinds of planar magnetron sputter guns with different magnetic field configurations and strengths. Using LPVD we have begun studies of alloy semiconductors such as CdZnTe and heavily doped semiconductors such as ZnTe:Cu for possible incorporation into CdTe-based photovoltaics.

The film properties have been studied by x-ray diffraction, scanning electron microscopy, and photoluminescence for a range of substrate temperature, substrate voltage bias, gas pressure, and rf power. For a wide range of growth conditions, we have determined crystallographic orientation, and grain morphology and size, as well as electrical and optical properties of the films. Other characterization measurements performed at UT include Raman, double-beam optical absorption, photoreflectance and electoreflectance, Hall effect, electrical conductivity, current-voltage (I-V), spectral quantum efficiency (SQE), and frequency-dependent capacitance-voltage (C-V) measurements.

Comparisons between the magnetron guns with unbalanced vs. balanced magnetic fields, based on Langmuir probe and optical emission measurements, show that the unbalanced gun produces a higher electron temperature (5 eV vs. 4 eV), about twice the electron density, twice the ion flux, and somewhat higher ion energies impacting the substrate. Cadmium sulfide and cadmium telluride films grown with the unbalanced gun yield much higher photoluminescence efficiencies, and the solar cells grown using the unbalanced gun for the CdTe layer have much better performance.

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1.0 Introduction

1.1 Background

This annual report covers the first year of a second three-year NREL contract with the University of Toledo which is focussed on improvements in efficiency for rf sputtered CdS/CdTe solar cells. This contract follows the initial one in which two deposition methods for CdTe film growth were explored--laser physical vapor deposition (LPVD) and rf sputtering (RFS).¹⁻⁷ In the first contract, the viability of the two deposition methods was established with the fabrication of solar cells exceeding 10% using either of the two techniques. Toward the end of the first contract, most of the effort was placed on RFS since it was judged to be more economical and more easily scaled to large area deposition. However, LPVD has remained our method of choice for the deposition of CdCl₂ layers and also for the exploration of new materials such as the ternary alloys including CdZnTe and dopants such as Cu in ZnTe.

1.2 Technical Approach

Plasma characteristics--In order to make significant advances in the performance of rf sputtered CdS/CdTe thin film solar cells, and to reach efficiencies in the range of 15%, it is important to obtain a thorough understanding of the fundamental science of the sputter-deposition process. Although a considerable amount of research effort has gone into the understanding of diode sputtering, the understanding of magnetron and particularly *rf* magnetron sputtering is less well understood. This is particularly the case for rf magnetron sputtering of II-VI semiconductor materials. Thus, during this year, a long-range effort was started to advance our understanding of rf magnetron sputtering of CdS and CdTe. In order better to understand the plasma and its interaction with the growing film, we have performed electrical measurements with a Langmuir probe and we have done optical emission spectroscopy of the plasma.⁸ We have examined especially the influence of the shape and strength of the magnetic field of the magnetron guns and also studied the effect of varying the substrate bias during deposition.

Materials characterization/device testing--After preparing films under a variety of conditions of sputter gas pressure, rf power, substrate temperature, and substrate bias, the resulting films were examined with several techniques. These included x-ray diffraction to determine the residual strain in the film and its dependence on substrate temperature and sputter gas pressure. Raman scattering and photoluminescence were regularly used to examine the film quality and particularly the types and quantities of radiative defects in the grains or grain boundaries. Scanning electron microscopy and energy dispersive x-ray spectroscopy were used to examine film morphology and composition. Finally, we used four-point probe and van der Pauw measurements of conductivity as well as Hall effect measurements of carrier concentration and mobility.

In addition to the studies of standard CdS and CdTe materials, during the past year we have begun studies of the ternary alloy semiconductor CdZnTe using LPVD for the film growth and

Raman, PL, x-ray, and electrical measurements for the film quality. In addition, we studied the effects of adding small pressures of oxygen to the growth chamber during LPVD growth of CdTe.

Other studies were done on completed devices. These included the usual I-V tests under illumination, spectral quantum efficiency, and frequency-dependent capacitance-voltage measurements.

Finally, a considerable effort was placed on improving the reproducibility of the entire cell fabrication process involving rf sputtering, laser deposition, CdCl₂ treatment, annealing, contact application, and diffusion.

2.0 Advances in Film Deposition and Cell Fabrication

2.1 Modifications to the sputter deposition facility

During the past year we constructed a new sputter chamber which is based on a six-way stainless-steel cross with eight-inch ports. See Figures 1 and 2. The chamber incorporates two magnetron sputter guns mounted in two opposing arms of the cross. The system utilizes a turbomolecular pump with pressure regulated by an exhaust valve controller and a capacitance manometer. The radiatively heated substrate is mounted via another port with a rotatable feedthrough which permits the substrate to be rotated from facing the first gun (typically CdS) to the second (typically CdTe) without interruption of the heater current. The substrate holder was electrically isolated from the heater and from the chamber walls to permit electrical bias to be applied during the deposition, if desired. An additional feedthrough was provided to accommodate a Langmuir probe for electrical measurements of the plasma properties. In addition, this chamber incorporates four small windows mounted at 45° permitting optical monitoring of the glass temperature and film thickness. Optical and electrical measurements are described below.

Fig. 2.1. Side view sketch of the two-gun sputtering chamber showing the pumping system, heater and substrate mounting, and sputter gun shutters.

Fig. 2.2. Top view sketch of chamber used for sequential sputtering of CdS and CdTe with four optical access ports used for *in situ* interference measurements of glass temperature and film thickness.

2.2 In situ interference measurements of glass substrate temperature

2.2.1 Background and instrumentation

The reliable measurement of radiatively heated glass substrate temperatures during the deposition of thin films poses significant challenges. The low thermal conductivity of glass causes difficulties in establishing thermal equilibrium between the glass and any mechanically contacted sensor. Furthermore, front-side contact exposes the sensor to the deposition flux and backside contact may shadow the glass from the radiative heating flux. Earlier we have used fluorescence from a small ruby chip attached to the glass and monitored the wavelength shift of the R_1 , R_2 red doublet. However, this method also suffers from some of the same problems as, e.g., thermocouple sensors, namely, film coating on the ruby, additional thermal mass, and change in

emissivity due to the sensor presence. A classic technique for glass temperature determination is optical pyrometry. However, for photovoltaics the deposition temperature is often below 400 C and the pyrometry must then be done in the infrared. This requires not only appropriate infrared-transmitting windows and knowledge of the emissivity of the glass and/or film surface, but also is subject to errors resulting from window transmission changes due to accumulating deposits on the window and emissivity changes due to film growth.

We have found that optical interference analysis using a small HeNe laser beam reflected from the back side of the glass substrate can give accurate and convenient measurements of glass temperature without disrupting the rf plasma.⁹ This method measures a combination of the thermal expansion of the glass and thermal changes in the index of refraction of the glass. The measurement is insensitive to window transmission changes but does require constant monitoring of the reflected beam while the glass is heated or cooled from a known reference temperature. Also, in situations where the glass is in motion for any part of the preheat time, this method will be significantly more difficult to implement.

In order to facilitate *in situ* optical measurements, we included four small optical access ports into the design of our new double-gun, rf sputtering chamber. The substrate is radiatively heated by a tantalum or Haynes metal wire heater behind the glass substrate. In order to accommodate the laser beam, the radiation shield behind the wire heater was slotted to permit the entrance and exit of the laser beam. Note that this chamber design permits the substrate and heater assembly to be rotated by 180° to change from the first to the second deposition while maintaining substrate temperature. The four windows at 45° to the axis of the sputter guns permit backside interference measurements in either position. An additional benefit is that this geometry permits *in situ* transmission measurements to monitor the film thickness *during* deposition. A small HeNe laser ($\lambda=633$ nm) worked well for the reflection measurements of glass temperature and also for the absorption measurement of CdTe film thickness. An argon laser line ($\lambda=458$ nm) was used for absorption measurements of CdS film thickness.

2.2.2 Fringe shift calibration

In order to calibrate the fringe shift vs. temperature, the various glasses were measured at near-normal incidence in air in a specially constructed thermal enclosure with a window for the entering and exiting beams. In this case the glass was placed directly on a hot stage and a Type K thermocouple was bonded with silver paint to the top surface of the glass. The thermocouple was placed within 1 cm of the point of incidence of the HeNe laser beam. Figure 2.3 shows the accumulated fringe count as a function of the substrate temperature for alkali-free glass, soda-lime glass, and for fused silica. The rate of fringe shift is, of course, linear in the glass thickness but varies with different glass compositions. The data are not explained simply by the different thermal expansion coefficients of the glasses. One must account also for the temperature dependence of the indices of refraction.

The precision needed for the temperature dependence of the index of refraction is one part in 10^6 and this is not available in the literature for these glasses over the temperature range needed for

PV film depositions. We have therefore measured this temperature dependence of the index of refraction using the hot stage and thermal enclosure described above.

Fig. 2.3. Number of fringe shifts observed as a function of glass temperature for $\lambda = 632.8$ nm with $\theta = 5^\circ$ for four different glasses. Data are normalized to 1 mm glass thickness.

2.2.3 Temperature dependence of glass thickness and refractive index

The well-known condition for an extremum in the interference from a film or plate of thickness d is given by

$$m\lambda = 2nd \cos \theta, \quad (1)$$

where θ is the angle of transmission in the film or plate, n is the index of refraction, and m is an integer. A shift of one fringe occurs when $\Delta m = \pm 1$, or

$$2(n\Delta d + d\Delta n) \cos \theta = \lambda, \quad (2)$$

where $\Delta d = \alpha d \Delta T$, $\Delta n = \gamma \Delta T$, θ is the angle of incidence, and α is the linear thermal expansion coefficient. The thermal coefficient of the index of refraction, γ , is composed of two terms, a direct temperature dependence of the index of refraction and an indirect term related to the density effect on the index of refraction. Thus

$$\gamma = dn/dT = \partial n / \partial T - \beta \rho \partial n / \partial \rho, \quad (3)$$

where ρ is the glass density and β is the volume coefficient of expansion [$\beta = 3\alpha = \partial V / (V \partial T)$]. The thermal expansion of the different glasses is shown in Fig. 2.4 where the data have been taken from the literature.¹⁰ The work described in this paper provides the needed values for γ .

Fig. 2.4: Thermal expansion data from Ref. 10 used for the analysis of the thermal dependence of the index of refraction.

The measured changes in the index of refraction with temperature (dn/dT) are shown in Figs. 2.5, 6, 7, and 8 for Corning 7059, NEG 0A-2, LOF soda-lime, and fused silica. Note that over the temperature range from 0 to 400°C the value of $\gamma = dn/dT$ is monotonically increasing with a linear dependence on temperature for all but the soda-lime glass. In this case, γ exhibits a significant quadratic component vs. temperature.

In general, γ may be fit by a quadratic function of the form

$$\gamma(^{\circ}\text{C}^{-1}) = A + B(T-T_0) + C(T-T_0)^2, \quad (4)$$

where, in our case $T_0 = 273$ K. The functions which fit the data of Figures 2.5-2.8 are summarized in Table 2.1.

Table 2.1: Temperature Derivative of n, $\gamma=dn/dT$				
	silica	7059	0A-2	LOF
$A(^{\circ}\text{C}^{-1})$	0.7524	4.272	5.414	2.167
$B(^{\circ}\text{C}^{-2})$	0.0317	0.0182	0.0149	0.0054
$C(^{\circ}\text{C}^{-3})$	0	0	0	8.4×10^{-5}

Fig. 2.5: dn/dT vs. T for Corning 7059 at 633 nm.

Fig. 2.6: dn/dT vs. T for NEG 0A-2 at 633 nm.

Fig. 2.7: dn/dT vs. T for LOF soda-lime glass at 633 nm.

Fig. 2.8: dn/dT vs. T for fused silica at 633 nm.

2.2.4 Discussion and interpretation

Note from Eq. 3 that the density change with temperature will yield a negative contribution to γ for cases in which the volume coefficient of expansion $\beta = (1/V)\partial V/\partial T$ is positive. Since the measurements which were used to calculate the values of dn/dT involve simply monitoring the fringe changes, the measurement does not directly yield the sign of γ . However, we have taken advantage of the $\cos(\theta)$ term in Eq. 1 to determine the relative sign. This involved comparison of the fringe change resulting from a small rotation of the glass with the fringe change caused by a small temperature change. dn/dT was found to be positive in all cases. Since dn/dT was found to be positive, the direct increase of index of refraction with temperature ($\partial n/\partial T$) at 633 nm is larger, apparently, than the density-dependent decrease ($-\beta p \partial n/\partial p$) for all of the glasses measured here.

The two parts to the index of refraction change with temperature (Eq. 3) arise in the following way: The indirect term arises from the fact that the index of refraction is directly proportional to the density of polarizable "molecular" units in the solid which decreases as the temperature rises (due to thermal expansion). Conversely the direct dependence of n on T arises from the facts that (1) the band gap in most solids decreases with increasing temperature and (2) the broadening of optical transitions increases with temperature. The real part of the index of refraction of these glasses has normal dispersion ($dn/d\nu > 0$) which is tied essentially to the onset of absorption in the ultraviolet. Thus a band gap decrease with increasing temperature produces a positive dn/dT which is largest for the soda-lime glass due to its smallest photon energy for onset of absorption. Furthermore the broadening with temperature also produces a positive dn/dT which, again, will be largest for the glass with the smallest optical gap.

There is existing index-of-refraction data in the literature for borosilicate glass which covers a similar temperature range as the work reported here. In Ref. 11, the index of refraction at $\lambda = 587.7$ nm was measured directly at four temperatures. The results at 20, 200, 400, and 600°C were, respectively $n = 1.4760, 1.4772, 1.4790, 1.4824$. The average values of dn/dT from these data agree very nicely with the data presented in Figs. 2.5 and 2.6 above.

As an illustration of the utility of this technique, we have measured the increase in substrate temperature after the sputter gun is ignited. We find the temperature increase to be 10 - 15 °C, for 120 W of rf power into the matching network of the 50 mm diameter gun 70 mm from the substrate.

2.3 Characteristics of the rf plasma for two magnetic field geometries

In the planar magnetron sputtering gun, the presence of a static magnetic field is used to modify the electron trajectories to enhance the ionization near the target, thus increasing deposition rates and permitting lower sputter gas pressures. In addition, the magnetic field may alter the electron flux incident on the growing film. (The magnetic field of the magnetron gun has a strong influence on the electron trajectories but little effect on the ion motions.) In many sputtering applications, mechanical properties such as adhesion and hardness or optical properties are the critical parameters of the deposited films.¹² Generally the electrical properties of sputtered films have not been studied extensively, particularly for the case of semiconductors. However, in the

use of sputtering for the deposition of photovoltaic films, optimizing the electrical properties is critical for achieving highest cell performance.

Sputtering is characterized by significant densities of ions and electrons ($\sim 5 \times 10^{10}/\text{cm}^3$ in the background of $\sim 4 \times 10^{14}/\text{cm}^3$ of neutrals at 18 mT); however, their influence on the electrical properties of the film is not well understood. In order to improve the quality of the polycrystalline thin films needed for high efficiency solar cell performance, and to take full advantage of the unique properties of magnetron sputtering including the electron and ion bombardment and large quantities of excited species in the growth flux, we have begun systematic studies of the plasma properties achievable with magnetron guns. As a starting point we have chosen to use two guns with quite different magnetic field characteristics.

One of the 50 mm diameter planar magnetron sputtering guns had an approximately balanced magnetic field¹³ and the other had a strongly unbalanced magnetic field.¹⁴ Substrates of borosilicate glass (Corning 7059 or NEG 0A2) or SnO_2 -coated soda lime glass (LOF 8 or 10 Ω/square) were held at a distance of 70 mm and heated radiatively with the serpentine wire heater. Glass temperature was checked by ruby fluorescence³ and by optical interference fringe counting.⁹ A sketch of the system showing the magnetic field distributions of the two guns is shown in Fig. 2.9. The figure shows schematically the erosion tracks on the target surfaces. The diameter of the erosion track was 1.15 in. for the balanced magnetron and 1.00 in. for the unbalanced magnetron. Note that in Fig. 2.9 and subsequent figure captions and legends we give rf powers in terms of power *supplied to the matching network*. We have measured the power dissipated in the matching network and estimate that the power *into the magnetron* is about 50% of this.

2.3.1 Optical emission spectroscopy

The strength and configuration of the magnetic fields of the two sputtering guns has a significant effect on the electron confinement and therefore also on the degree of excitation and ionization in the plasma at some distance from the sputter guns. This is illustrated by the plot of emission intensity of the neutral Cd emission at 508.6 nm shown in Fig. 2.9, Panel c. Note that although the two guns generate very similar light emission intensities for the Cd line very near the gun--at 6 mm from the target surface), the unbalanced gun generates much higher light emission at large distances.

We have studied several emission lines in the plasma. Among these are neutral Ar (518.8 nm), neutral Cd (508.6 nm), and ionized Ar (488.0 nm). The intensity dependence of these emission lines on distance from the sputter target is shown in Figures 2.10 and 2.11 for the unbalanced and balanced guns respectively. In general the unbalanced gun generates much higher densities of excited state species several centimeters from the sputter gun source. This is true of both the sputter gas (Ar) and sputtered atoms (e.g., Cd).

As an example of the light emission along a line perpendicular to the centerline of the sputter target and the substrate and at a distance of 67 mm from the target, Fig. 2.12 shows the Cd (508.6 nm) intensity behavior for the two guns. Note that the light emission from the balanced-magnetron-generated plasma is weaker and less peaked along the centerline.

Fig. 2.9: Magnetic field structure of (a) unbalanced and (b) balanced field planar magnetron sputter guns used in this work. The left side shows top views of sputter gun heads with central magnets and a ring of magnets for the unbalanced gun (a) or an annular magnet for the balanced gun (b). The right side shows side views of sputter gun - substrate arrangements. Magnetic field strengths, measured with a Bell model 615 gaussmeter, are shown in Gauss. Panel (c) shows the optical emission signal, obtained with a PAR OMA-II vidicon and 1/4 meter Aries spectrometer, for the CdI line at 508.6 nm at 18 mTorr and 120 W of rf power.

Fig. 2.10: Optical emission intensity vs. distance from a CdTe sputter target for the *unbalanced* magnetron gun at 120 W of rf power and argon pressure of 18 mTorr.

Fig. 2.11: Optical emission intensity vs. distance from a CdS sputter target for the *balanced* magnetron gun at 120 W of rf power and argon pressure of 18 mTorr.

Fig. 2.12: Optical emission intensity of Cd-I (508.6 nm) at 67 mm from the CdS sputter target (5 mm from substrate) at 150 W of rf power and 18 mTorr pressure of Ar. Distance measured perpendicularly from centerline of target-substrate.

2.3.2 Langmuir probe measurements

The light emission from the plasma gives clear indication that significant densities of excited state atoms and ions are present, indirectly indicating the presence of energetic electrons needed for atomic excitation. A more direct measure of the electron and ion densities and of the electron temperature can be obtained with Langmuir probe measurements. Because this is a somewhat invasive technique, the probe wire must be kept short and thin. The Langmuir probe was placed 1 cm from the substrate on the center line of the substrate-target system. (See Figure 2.1.) The probe consisted of a 0.13 mm diameter tantalum wire with 5 mm exposed beyond the end of a glass capillary sheath. With these dimensions and modest probe biases, the probe is not expected to affect significantly the behavior of the plasma. The probe was oriented parallel to the substrate, crossing the centerline of the target-substrate, at a distance of 10 mm from the substrate and 60 mm from the sputter gun target. At this position the magnetic field is about 30 G and 2 G, respectively, from the unbalanced and balanced guns. For a 30 G field the electron gyro-radius is about 3 mm, much larger than the probe diameter (or even the space-charge sheath diameter) so that the effect of the magnetic-field on the current collection can be neglected.

Figure 2.13 shows the current-voltage characteristics of the Langmuir probe in the plasma generated by the balanced magnetron gun for three argon gas pressures. Details of the shape of such an I-V curve are discussed in the literature. We briefly summarize some key aspects referring to Figure 2.13 for some of the characteristic regions of the curve.

Fig. 2.13: Current-voltage characteristic of the Langmuir probe in plasma from the balanced magnetron gun (CdTe target) at 150 W of rf power and argon pressure of 5 mTorr. a) linear axes; b) semi-logarithmic plot.

In the region BC, the probe potential, V_p , is somewhat more negative than the plasma potential, V_p . Here the electron current, I_e , is given by

$$I_e = I_e^* \exp[-e(V_p - V_b)/kT_e], \quad (1)$$

where T_e is the electron temperature, and I_e^* is the electron saturation current. Thus a logarithmic plot of I-V curve in this region can yield the electron temperature from the slope and the plasma potential from an intercept,

$$\ln(I_e) = -e(V_p - V_b)/kT_e + \ln(I_e^*). \quad (2)$$

The ion current is related to the Bohm criterion

$$I_i = 0.6 n_e S (kT_e/m_i)^{1/2}, \quad (3)$$

where m_i is the ion mass, n_e is the electron density, and S is the area of the ion sheath boundary. The point at which the current vanishes yields the probe floating potential, V_f . At this point the electron current is balanced by the positive ion current. Equating the ion and electron currents defines the floating potential ($V_f \equiv V_b$) and yields

$$V_p - V_f = (kT_e/2e) \ln(m_i/2.3m_e). \quad (4)$$

Thus, for Ar ($m_i=40$), we have

$$V_p = V_f + 4.7 kT_e/e. \quad (5)$$

For values of probe potential significantly larger than the plasma potential (region AB in Fig. 2.13), the ion current vanishes. The electron current increases in a more complicated way related to the increasing area of the sheath of negative space charge surrounding the probe. We have approximated this behavior with a straight line fit on the logarithmic plot, as is commonly done, for modest positive probe voltages. (In our case the probe current begins to increase rapidly above $V_b \sim 60V$ as the probe maintains a self-sustained discharge presumably due to secondary electron emission.) The intersection of these two logarithmic dependences is often taken to be the plasma potential. For the numbers given in Table 2.1 we have used Eq. 5, which agrees reasonably well with the graphical values.

Fig. 2.14: I-V curves for Langmuir probe at three rf powers and argon pressure of 18 mTorr. CdS target. a) Unbalanced sputter gun (AJA); b) balanced sputter gun (KJL).

Figure 2.14 gives the Langmuir probe I-V curves for three different rf powers for the two sputter guns using CdS targets and argon sputter gas pressure of 18 mT. Figure 2.15 gives the I-V curves obtained for the two guns for three different argon gas pressures at an rf power of 150W. These curves form the basis for the plasma parameters which are summarized in Table 2.2. The last figure showing I-V characteristics displays the effect on the plasma of applying a bias to the substrate. Fig. 2.16 demonstrates that a negative substrate bias has little effect on the plasma

characteristics but that a positive bias effectively raises the plasma potential. This behavior is readily explained by the fact that the plasma potential is determined by the most positive anode surface. Normally this is the chamber walls at ground potential. However, the substrate and its holder assembly constitute a surface area which is close enough and large enough to control the plasma potential when positive bias is applied. Effectively the positively biased substrate attracts enough electrons to raise the plasma potential and reestablish the substrate-plasma sheath at its usual value. Therefore positive substrate biases do not change the ion energies at the substrate surface. Negative biases, however, will increase the ion energies since the plasma potential is fixed by the (more positive) chamber walls. These effects are clearly shown in x-ray diffraction studies of the crystal quality, as discussed below.

Fig. 2.15: I-V curves for Langmuir probe for three argon pressures and rf power of 150 W. CdS target. a) unbalanced magnetron (AJA); b) balanced magnetron (KJL).

Fig. 2.16: I-V curves for Langmuir probe for 150 W or rf power, 18 mTorr of argon, unbalanced magnetron gun and three different *substrate* biases. Unbalanced magnetron; CdS target.

A summary of the plasma characteristics is given in Table 2.2. Note that the unbalanced magnetron has higher electron density and temperature, higher ion flux onto the substrate, and somewhat higher substrate sheath potential, $V_p - V_{sb}$, the acceleration potential of ions across the substrate sheath for the case of a substrate at floating (self-bias) potential. In addition to the higher electron flux, note that the unbalanced gun yields a higher ratio of positive-ion-to-neutral Cd+S flux. The data presented below show that these differences in plasma characteristics also affect the quality of the as-grown CdS and CdTe films.

Table 2.2: Unbalanced vs. Balanced Magnetron Characteristics ($P_{RF} = 150$ W, $p_{Ar} = 18$ mT, CdS Target)		
	UNBALANCED	BALANCED
substr. self bias, V_{sb}	-2.2 V	+8 V
plasma potential, V_p	+25 V	+29 V
substr. sheath, $V_p - V_{sb}$	+27 V	+21 V
ion flux, $F_I(\text{cm}^{-2}\text{sec}^{-1})$	1.8×10^{15}	1.0×10^{15}
deposition flux, $F_{Cd+S}(\text{cm}^{-2}\text{sec}^{-1})$	2.4×10^{15}	2.6×10^{15}
F_I/F_{Cd+S}	0.75	0.4
electron temp., T_e	5.3 eV	4.0 eV
electron density, $n_e(\text{cm}^{-3})$	7.6×10^{10}	3.9×10^{10}

2.4 X-ray diffraction studies

In order to examine further the effects of the different plasma characteristics on the film quality, we compared the structural properties (via x-ray diffraction and SEM), electrical properties, and photoluminescence properties of individual films of CdS and CdTe grown with the two sputter guns having the magnetic field characteristics shown in Fig. 2.9. With the design of the new two-sputter-gun chamber, it is possible to apply an electrical bias to the substrate during growth. Section 2.3 above showed that positive substrate bias causes the plasma potential to rise with no substantial change in the substrate sheath potential. However, with negative bias applied to the substrate, it is possible to increase the substrate sheath potential. We have used x-ray diffraction to observe changes in the lattice spacing perpendicular to the substrate, and also possible changes in the cubic to hexagonal ratio.

2.4.1 CdS

We have studied CdS films sputter deposited on both borosilicate glass and on SnO_2 -coated soda-lime glass. The results were similar. Here we present the x-ray diffraction results for CdS on the SnO_2 -coated LOF glass. Figure 2-17 displays the diffraction spectra for three films grown with the unbalanced magnetron gun. One was grown with standard conditions (no bias, $T_s=380^\circ\text{C}$), one with -50V substrate bias and $T_s=380^\circ\text{C}$, and one with -50V bias at 200°C . Both CdS and SnO_2 peaks are identified in the diffractograms. The bias broadens the CdS peaks with the effect most apparent on the peak from the higher index plane $\langle 103 \rangle$ at 47.7° . However, the other peaks also are broadened. The lower temperature growth shows somewhat more broadening on all of the lines than growth at 380°C . For the balanced magnetron gun, the diffractograms of Fig. 2-18 show similar broadening when a bias of -50V is applied to the substrate during growth. In this case there appears to be some evidence that the peaks are slightly narrower for the 200°C growth (without bias) than for the 380°C growth. We conclude that the increased ion energy (mainly Ar^+) impacting the substrate causes the crystalline damage responsible for the broader peaks. Note from Fig. 2.16 and Table 2.2 that the usual substrate sheath potential is 27 V for the unbalanced gun and 21 V for the balanced gun but this is increased to 75 V and 79 V , respectively when a d.c. bias of -50 V is applied to the substrate. We note that, as expected, there was no observable change in the diffraction patterns observed for films grown under positive bias since the substrate sheath potential is hardly affected by positive biases on the substrate. See Figure 2.16 above.

2.4.1 CdTe

In the case of CdTe films, we have studied the lattice structure of single films on both borosilicate glass and on SnO_2 -coated soda-lime glass. However, in this case we are able also to study x-ray diffraction from completed cell structures before and after treatment with CdCl_2 . Diffraction studies have been made on films grown at room temperature, 200°C , and 380°C , with and without a substrate bias of -50 V . All films were grown with the unbalanced magnetron gun. The films grown without bias have a very strong $\langle 111 \rangle$ crystallographic texture as seen by the data of Figs. 2-19 and 2-20. However, there is some observable diffraction from cubic phase

Fig. 2.17: Cu K_{α} x-ray diffraction spectra from CdS films grown on SnO_2 -coated soda lime glass using 150 W of rf power from the *unbalanced* magnetron gun. a) $T_s=385\text{C}$, no substrate bias; b) $T_s=385\text{C}$, -50 V substrate bias; c) $T_s=200\text{C}$, -50V substrate bias.

Fig. 2.18: Cu K_{α} x-ray diffraction spectra from CdS films grown on SnO_2 -coated soda lime glass using 150 W of rf power from the *balanced* magnetron gun. a) $T_s=385\text{C}$, no substrate bias; b) $T_s=385\text{C}$, -50 V substrate bias; c) $T_s=200\text{C}$, no substrate bias; d) $T_s=200\text{C}$, -50V substrate bias.

Fig. 2.19: Cu K_{α} x-ray diffraction spectra from CdS/CdTe solar cells grown on SnO_2 -coated soda lime glass using 150 W of rf power from the *unbalanced* magnetron gun. a) $T_s=200^\circ\text{C}$, no substrate bias; b) $T_s=200^\circ\text{C}$, -50 V substrate bias. Peaks labelled C (H) corresponds to the cubic (hexagonal) form of CdTe.

Fig. 2.20: Cu K_{α} x-ray diffraction spectra from CdS/CdTe solar cells grown on SnO_2 -coated soda lime glass using 150 W of rf power from the *unbalanced* magnetron gun. a) $T_s=385^\circ\text{C}$, no substrate bias; b) $T_s=385^\circ\text{C}$, -50 V substrate bias. Peaks labelled C (H) correspond to the zincblende cubic (wurtzite hexagonal) phases of CdTe.

crystallites with other orientations and, additionally, evidence of regions of hexagonal structure. This is consistent with observations made by others on sputtered CdTe films.^{16,17} As seen with CdS films, the presence of a negative 50 V substrate bias serves to broaden the diffraction peaks, probably due to Ar⁺-ion-induced bombardment damage and/or ion-bombardment-induced microscopic strain. The full width at half maximum of the <111> peak at 23.8° is $\Delta(2\theta) = 0.08 - 0.09$ degrees for growth at 380 C. The linewidth is almost a factor of two broader for films grown at 200 C or at room temperature.

It should be noted that the rf sputtered films show a larger-than-normal <111> interplanar separation in the as-grown condition. After CdCl₂ treatment and anneal at 400 C in air, some of the strong <111> lattice texture is lost and there is some reduction in the <111> lattice constant. This indicates that the rf sputtered films are in compression (in the film plane).^{17,18} Treatment with CdCl₂ and anneal helps to relieve this stress. We have studied several films grown with different sputter gas pressures and substrate temperature. The results of these studies are shown in Figures 2.21 and 2.22. Figure 2.21 shows that films grown at room temperature exhibit little lattice strain, possibly related to the fact that the grain size is very small for room temperature growth. Strain is approximately constant at 3% ($\Delta a = 0.011$ Å relative to CdTe powder) for growth above 200 C. The application of a substrate bias of -50 V produces some additional strain.

Fig. 2.21: Substrate temperature dependence of the <111> lattice constant in CdTe films grown on borosilicate glass using the unbalanced magnetron gun at 120 W of rf power and Ar gas pressure of 18 mTorr. Lattice constant (3.742 Å) for CdTe powder is indicated by the arrows. Dashed curve is only a guide for the eye.

Fig. 2.22: Dependence of CdTe <111> lattice constant on Ar sputter gas pressure for unbalanced magnetron and $T_s = 310 - 385$ C. Solid lines are polynomial fits to the data.

After CdCl_2 -treatment and anneal at 400 C, the as-grown strain is substantially reduced.^{17,18} Fig. 2-22 shows this relaxation as well as the dependence of strain on the Ar sputter gas pressure. Note that the strain can be reduced from 4.4% at 2.3 mTorr growth pressure to 2.5% at a growth pressure of 50 mTorr.

2.4.3 Relationship between film blistering, strain, and substrate bias

In our annual report for last year³ we reported on problems with blistering of some solar cells after the CdCl_2 treatment and 400 C anneal. We now understand that this blistering was primarily caused by the fact that negative bias during the deposition of CdS increases microscopic strain and damage. We discovered that the heater and substrate holder assembly which we constructed for the new double-gun sputtering chamber had been slightly damaged at one point so that the substrate holder was shorted to the ungrounded side of the tantalum heater wire. This was causing the substrate to receive an a.c. bias of about $V_{\text{rms}} = 17$ V when a substrate temperature of 380 C was used. Although, as we discussed above, a positive bias does not have much effect on the growing film, the negative-going half cycle causes additional substrate sheath potential which increases the Ar^+ ion energies impacting the growing film. This additional ion energy is enough to cause strain sufficient to lead to blister formation during the post-deposition treatment. Removing the short cleared up the blistering problem. We have also found that sputtering at higher gas pressures, reducing the thickness of CdTe, and using less CdCl_2 can reduce the tendency of the CdTe film to blister when deposited onto CdS.

2.5. Photoluminescence studies

The radiative decay associated with electron-hole recombination is a very powerful tool for investigating the materials quality of semiconductor films. We regularly use photoluminescence for monitoring film quality--for example, as a function of the substrate growth temperature. Here we report on studies of the film quality as a function of the type of sputter gun used for the film growth. In particular we focus on the dependence on the two different magnetic field configurations and on the effects of applying a d.c. bias to the substrate during the film growth. All PL results given below were obtained on films held at liquid nitrogen temperature.

2.5.1 CdS

Figure 2.23 shows a comparison between the photoluminescence observed from CdS films grown with these two sputtering guns but with otherwise identical growth parameters. The growth rates for the two guns were nearly the same; both films were deposited on $8\Omega/\square$ SnO_2 -coated glass from LOF. The CdS film grown with the unbalanced gun exhibits approximately 1000 times stronger photoluminescence than the film grown with the balanced magnetron gun. In general, films grown with the unbalanced gun exhibited strong near-band-edge PL at 500 nm indicating relatively few deep traps, whereas films grown with the balanced gun show very weak PL from a band of radiative centers relatively deep in the gap (~ 250 meV lower photon energy). The weakness of the PL indicates a high density of nonradiative recombination centers. We believe that the improved quality of films grown with the unbalanced magnetron is due to the enhanced flux of low energy electrons, ions, and/or excited atoms onto the substrate during growth with the unbalanced magnetron.

Fig. 2.23: PL at 80K from two CdS films on $8\Omega/\square$ SnO_2 . SC-70 grown with balanced, and SC-75 grown with unbalanced magnetron; $P_{\text{rf}}=150\text{W}$, $T_s = 385\text{C}$, $p = 18$ mTorr, $\lambda_{\text{ex}} = 458$ nm. Line structure in upper trace is Raman scattering. This is masked in the lower trace by the very strong PL. The same CdS target was used for both films with at least 15 minute target conditioning before films were deposited.

Further evidence that the ion impact energies are important in determining the PL efficiency and spectral features is provided by Figs. 2-24 and 2-25. In these figures we present, for each gun, a comparison of the PL from films grown with the substrate unbiased and with the substrate biased at -50 V d.c. Note that for films grown with the unbalanced magnetron, the application of the negative substrate bias reduces the near-band-edge emission peak at 475 nm by about a factor of 20 and shifts the deep level emission further toward the red. It should be noted that thin-film interference effects can modify the shape of broad emission bands so that care must be used in interpreting the various peaks apparent in the spectra. Effort is under way at resolving these effects. Nevertheless, the effect of bias is quite dramatically apparent.

In the case of the balanced magnetron sputter gun, the CdS films exhibit weak PL when the substrate is unbiased and the application of a -50 V substrate bias during film growth has a much smaller effect on the PL. In fact, because the PL is so weak, the spectra are dominated by the Raman scattering. The fact that multiple-order Raman scattering is observed with up to 7 overtones, indicates that the film quality is reasonably good, although the balanced magnetron films are even higher. Because the spectra were taken with 10 Å step size, the Raman peak heights are not accurate since their intrinsic width is small. Nevertheless it is clear that the overtone intensity decreases faster in the film deposited with -50 V bias. Thus the trend is similar to that observed with the films deposited from the unbalanced magnetron.

Fig. 2-24: 80K, 4579 Å excited Raman and PL from *unbalanced* magnetron CdS films on SnO₂ grown at 18 mTorr, $T_s=385^\circ\text{C}$, and 150 W of rf power. Upper trace -50V bias (CS75), lower trace no bias (CS76).

Fig. 2-25: 80K, 4579 Å excited Raman and PL from *balanced* magnetron CdS films on SnO₂ grown at 18 mTorr, $T_s=385^\circ\text{C}$, and 150 W of rf power. Upper trace unbiased (CS70), lower trace -50 V bias (CS71).

2.5.2 CdTe films and solar cells

As-deposited films of CdTe exhibit very little PL unless the growth temperature is near 400 C or above. Therefore, we show below the PL from CdTe after the post-growth process of CdCl_2 deposition (by LPVD) and air anneal at 400 C. We find that even after these treatment steps, the CdTe layers show strong differences related to the type of sputter gun which was used for the deposition. All studies reported below were made on complete solar cell structures (adjacent to back-contact metallizations). Spectra are shown both for the laser excitation from the air (vacuum) side as well as from the glass/ SnO_2 /CdS side.⁶ To facilitate these studies through the glass, we utilized the 752 nm line from a Kr laser. Thus, in some of the films, Raman scattering is seen together with the PL.

Figure 2.26 compares the PL from the CdTe/air side for cells prepared with the unbalanced gun and the balanced gun. Similar to the CdS films, the CdTe deposited with the balanced gun shows that the PL is almost completely suppressed--even after the CdCl_2 + heat treatment. The spectrum is similar to that observed from an as-grown film. The CdTe grown with the unbalanced gun, however, shows a very strong PL signal with a near-band-edge peak at 800 nm and a deeper band near 860 nm. Data are not corrected for spectrometer response which fall significantly for $\lambda > 8700 \text{ \AA}$.

Fig. 2.26: PL from CdTe observed at 80K, excited with $\lambda=752 \text{ nm}$ Kr laser line. The two traces compare the PL from the CdTe/air surface of two cells with CdTe grown from the unbalanced magnetron (SSC-119) and from the balanced magnetron (SSC-178) Raman lines are obscured by the much stronger PL in the case of the unbalanced-gun grown CdTe. Target was conditioned 2-3 hours before film growth.

Figure 2.27 shows the effect of maintaining a -50 V bias during the CdTe deposition with the unbalanced gun. PL signal was obtained from the CdTe/air interface. Two effects are evident: a shift in the near-band-edge peak and some reduction and some red shift and intensity decrease in the deep-level band.

Figure 2.28 shows the effect of maintaining a -50 V bias during the CdS deposition. The CdS layer was deposited with the balanced gun and the CdTe layer was deposited with the unbalanced gun (with no substrate bias). In this case the PL excitation was done with 458 nm so that signal arises mainly from the CdS/CdTe interface region. (The 458 nm light has an absorption length in CdS of $1/\alpha = 0.12 \mu\text{m}$ so that excitation is confined to the interface layer.) Again there are substantial differences between the two solar cell structures which appear to be related to differences in the amount of interdiffusion at this interface. However, a full interpretation has not yet been done.

Fig. 2.27: 80K PL from solar cell structure after CdCl_2 processing and anneal. 752 nm excitation on CdTe/air interface. CdTe deposited with *unbalanced* magnetron.

Fig. 2.28: 80K PL from solar cell structure after postdeposition processing. 458 nm excitation through glass/ SnO_2 . CdTe deposited with *unbalanced* magnetron.

2.6 SEM studies of microstructure

Our development of rf sputtering for the deposition of CdS and CdTe with high materials quality has been aided considerably by extensive use of scanning electron microscopy. Here we present an overview of some of our microstructure studies with the emphasis on qualitative aspects of the surface morphological changes which occur with increasing substrate temperature, with increasing sputter gas pressure, and with different magnetron magnetic fields. In the following discussion, we shall refer to various temperature regions based on the ratio of substrate temperature to the melting temperature, T_s/T_m . Such a model was first proposed by Movchan and Denchishin¹⁹ and extended by Thornton²⁰ to the case of d.c. magnetron sputtered metal films. This model appears to explain many of the phenomena we observe in the rf magnetron sputtered II-VI semiconductor films as well.

For room temperature deposition of CdTe, $T_s/T_m = 300\text{K}/1364\text{K} = 0.22$, which lies in the "zone 1" region of Thornton where diffusion of adatoms is negligible and atom shadowing effects dominate. Columnar growth occurs with columns oriented along the direction of the incident flux and generally with significant void space between columns. Many of these features are consistent with the plan-view micrographs shown in Fig. 2.29. On borosilicate glass the graininess has a typical length scale of ~ 100 nm and on the $10 \text{ } \Omega/\square$ SnO_2 -coated soda lime glass this structure persists, but now it is modulated by the underlying substrate morphology so that a "cauliflower-like" structure appears. Similar morphology appears with growth of CdS on SnO_2 -coated soda-lime glass.

At $T_s = 310 \text{ }^\circ\text{C}$, $T_s/T_m = 0.43$ and somewhat larger and more tightly packed grains appear (See Fig. 2.30.) with some evidence of faceting. This is a typical "zone 2" structure with enough adatom mobility to minimize surface energy and form true grain boundaries. At $T_s = 380 \text{ }^\circ\text{C}$, $T_s/T_m = 0.48$ and considerable faceting and grain growth occurs. Faceting and grain growth are further enhanced at $425 \text{ }^\circ\text{C}$ ($T_s/T_m = 0.51$).

Cross-sectional views are shown in Fig. 2.31 for as-deposited samples grown at room temperature, and $425 \text{ }^\circ\text{C}$; and for a sample grown at $200 \text{ }^\circ\text{C}$ and subsequently treated with CdCl_2 and annealed in air at $400 \text{ }^\circ\text{C}$. Pronounced columnar growth can be observed at $25 \text{ }^\circ\text{C}$ although the apparent columnar grains are probably quite porous, as indicated by Raman linewidth broadening. At $425 \text{ }^\circ\text{C}$ some evidence of the equiaxed structure appears, characteristic of growth in a "zone 3" region. (It should be noted, however, that Thornton indicates equiaxed structure occurs typically above $T_s/T_m \approx 0.7$ for magnetron sputtered metal films.)

The effect of sputter gas pressure is shown in Fig. 2.32 for CdTe sputtered on SnO_2 -coated soda-lime glass at $T_s = 310 \text{ }^\circ\text{C}$. At low gas pressures the films are dense and smooth, which is characteristic of the "zone T" structure of Thornton. The films grown at low gas pressure show the effects of the reduced atom and ion scattering in the plasma and the consequent increase of ion and atom bombardment of the film.

Fig. 2.29a: Plan-view SEM
of CdTe on borosilicate glass.
 $T_s=25^\circ\text{C}$; $p=18\text{ mTorr}$;
 $P_{\text{rf}}=120\text{W}$; $t=0.9\text{ }\mu\text{m}$.

Fig. 2.29b: SEM of SnO_2 -
coated soda lime glass (LOF),
 $10\text{ }\Omega/\square$.

Fig. 2.29c: SEM of CdTe on
 $10\text{ }\Omega/\square$ soda lime glass.
 $T_s=25^\circ\text{C}$; $p=18\text{ mTorr}$;
 $P_{\text{rf}}=120\text{W}$; $t=0.83\text{ }\mu\text{m}$.

Fig. 2.30a: SEM of CdTe on $10\Omega/\square$ soda lime glass.
 $T_s=310^\circ\text{C}$; $p=18\text{ mTorr}$;
 $P_{\text{rf}}=120\text{W}$; $t=1.06\mu\text{m}$.

Fig. 2.30b: SEM of CdTe on $10\Omega/\square$ soda lime glass.
 $T_s=380^\circ\text{C}$; $p=18\text{ mTorr}$;
 $P_{\text{rf}}=120\text{W}$; $t=0.81\mu\text{m}$.

Fig. 2.30c: SEM of CdTe on $10\Omega/\square$ soda lime glass.
 $T_s=425^\circ\text{C}$; $p=18\text{ mTorr}$;
 $P_{\text{rf}}=120\text{W}$; $t=1.2\mu\text{m}$.

Fig. 2.31a: Fracture cross section SEM of CdTe on $10\Omega/\square$ soda lime glass. $T_s=25^\circ\text{C}$; $p=18$ mTorr; $P_{\text{rf}}=120\text{W}$; $t=0.83\mu\text{m}$.

Fig. 2.31b: Fracture cross section SEM of CdTe on $10\Omega/\square$ soda lime glass. $T_s=425^\circ\text{C}$; $p=18$ mTorr; $P_{\text{rf}}=120\text{W}$; $t=1.2\mu\text{m}$.

Fig. 2.31b: Fracture cross section SEM of a solar cell after CdCl_2 treatment and 400°C anneal. $T_s=200^\circ\text{C}$; $p=18$ mTorr; $P_{\text{rf}}=120\text{W}$; $t=1.6\mu\text{m}$.

Fig. 2.32: SEM of CdTe on $10\Omega/\square$ soda lime glass for four Ar sputter gas pressures. $T_s=380\text{C}$; $P_{\text{rf}}=120\text{W}$; a) $p=3\text{mT}$, b) $p=10\text{ mT}$, c) $p=18\text{ mT}$, d) $p=50\text{ mT}$.

The final series of SEM micrographs, Fig. 2.34, shows some evidence of different morphologies between CdS films grown with a balanced magnetron and an unbalanced magnetron. These films were grown at 405°C ($T_s/T_m = 678\text{K}/1750\text{K} = 0.39$) and 18 mTorr pressure on borosilicate glass. The temperature ratio of 0.39 places this growth in the intermediate region between zones 1 and 2, which Thornton has identified as a possible "zone T" region which can be produced by ion bombardment in sputter deposition. Comparison of these two micrographs indicates typical zone 1 structure for the film from the balanced magnetron but a smooth, mirror-like film characteristic of zone T structure from the unbalanced magnetron. We infer that the more intense and energetic ion and electron fluxes onto the growing surface from the unbalanced magnetron is responsible for this difference. (See other comparisons between the two magnetrons in Sections 2.3, 2.4, and 2.5.) Other differences between films deposited with the balanced and unbalanced magnetron guns are still being investigated. A more comprehensive report of optical and Langmuir probe measurements as well as SEM studies will be included in the Ph.D. dissertation of Meilun Shao.

Fig. 2.33a: SEM of CdS on borosilicate glass grown with *balanced* magnetron. $T_s=405^\circ\text{C}$; $P_{\text{rf}}=120\text{W}$; $p=18\text{mTorr}$; $t=0.45\text{ }\mu\text{m}$.

Fig. 2.33b: SEM of CdS on borosilicate glass grown with *unbalanced* magnetron. $T_s=405^\circ\text{C}$; $P_{\text{rf}}=120\text{W}$; $p=18\text{mTorr}$; $t=0.83\text{ }\mu\text{m}$.

2.6. Cell performance--dependence on magnetron magnetic field

We have prepared solar cells using combinations of these two types of sputter guns and find that cell performance is seriously degraded when the CdTe layer is deposited with the balanced magnetron gun. The cell performance is less seriously affected when the CdS layer is grown with the balanced gun. These differences are consistent with the poor PL observed in as-grown films from the balanced gun. In typical CdS/CdTe cells, electron beam induced current (EBIC) measurements show that most of the carrier collection arises from the CdTe layer. Not surprisingly, depositing high quality CdTe, with long minority carrier lifetimes, is critical to obtaining high cell performance. The balanced magnetron films show much poorer overall photoluminescence in both the CdTe and the CdS films. The CdS PL characteristics especially show that the balanced magnetron gun yields films with low efficiency for near-band-edge emission suggesting that the minority carrier lifetime is poor.

We made one test to compare the effect on solar cell performance of the use of two different magnetic field magnetrons for the two semiconductor layers, CdS and CdTe. Thus, one cell was prepared in the two-gun chamber using the combination of the balanced magnetron for the CdS layer and the unbalanced magnetron gun for the CdTe layer. Then the guns were cleaned, targets interchanged and a cell was prepared using the unbalanced gun for CdS and the balanced gun for the CdTe layer. The erosion tracks have slightly different diameters; 1.00/1.15 inch for the unbalanced/balanced magnetrons (*cf.* p11). The targets were conditioned for at least two hours by growing films at normal rf power before these cells were made. Deposition temperature was held constant at 380 C, argon pressure was fixed at 18 mTorr, and magnetron rf power at 150 W for CdS and 120 W for CdTe. The CdS layer thickness was 0.4 μm and CdTe layer thickness was 1.8 μm . We found that if the CdS is deposited with the balanced magnetron and the CdTe with the unbalanced magnetron, the measured cell parameters were good ($\sim 10\%$ efficiency). If the CdS is deposited with the unbalanced magnetron and the CdTe with the balanced magnetron, the cell performance was very poor ($< 3\%$ efficiency). The results are summarized in Table 3 below. [It should be noted that cell performance has been optimized over the previous nine months in the first configuration and it is quite possible that changes in sputter deposition parameters and/or post deposition processing would improve the cell efficiencies obtained with the second gun configuration.] We have earlier reported a 10.4% efficient, all-sputtered cell grown with a single-gun chamber.² This effort utilized the unbalanced magnetron gun and is consistent with the present indications of poorer quality produced with a balanced gun.

Table 3.1: Cell performance vs. magnetron magnetic field

CdS (0.4 μm) CdTe (1.8 μm)	balanced unbalanced (SSC-164)	unbalanced balanced (SSC-179)
V_{oc}	0.794 V	0.619 V
J_{sc}	20.9 mA/cm ²	5.5 mA/cm ²
FF	0.679	0.48
η	11.3%	1.64%

As a consequence of these PL studies and the cell performance differences discussed above, we are now acquiring a second 2-inch magnetron of the unbalanced type. This vendor provides some flexibility to change the magnetic field configuration by changes in the permanent ceramic magnets in the sputter gun head. We anticipate improvements in performance when unbalanced magnetrons are used for *both* semiconductor layers and when sputter deposition parameters are fully optimized. Adjustable parameters include the substrate bias, substrate temperature, gas pressure, magnetron magnetic fields, and rf power.

3.0 Advances in materials characterization

3.1 A capacitance-voltage measurement system

During the past year we have instrumented a new admittance (including capacitance-voltage) measurement system. The system is based on a Stanford Research Systems SR-510 lock-in amplifier. The lock-in is controlled by an RS 232 interface from a personal computer which also uses a PCLabs PCL-812 interface card to automate the measurements. A mixer/buffer and a current-to-voltage converter are used as described in the block diagram of Fig. 3.1. The PCL-812 controls a relay which inserts a carbon resistor to calibrate the system for stray impedances at each new frequency. The lock-in signal then can be used to compute the complex impedance

Fig. 3.1: Block diagram of admittance vs. voltage system with a frequency range from 0.5 Hz to 100 kHz. Calibration resistance R_0 is automatically switched in at every new frequency.

of the device under measurement. We have tested the system over the frequency range from 0.5 Hz to 100 kHz. This system is presently being used for testing a range of solar cells we have fabricated and to correlate the C-V behavior and the C vs. frequency (C-v) characteristics with I-V and SQE characteristics of devices. In addition, we are including various materials characterization measurements such as PL and Raman scattering, Hall effect, SEM, x-ray diffraction, and optical absorption to find the materials and device characterization methods most sensitive to the final device performance.

As an illustration of the performance of the system, we show in Fig. 3.2a the C vs. V characteristics at 500 Hz of a 10.4% efficient sputtered CdS/CdTe solar cell. For reference, the inferred depletion width for an assumed constant doping density is shown along the right scale. In Fig. 3.2b we show the $1/C^2$ vs. V which in the dark follows a straight line appropriate for a depletion region having constant doping density. With an illumination current equivalent to 0.2 suns the capacitance increases significantly as a consequence of a reduced depletion width under illumination.

To illustrate the frequency capability of the system, we show in Fig. 3.3 the frequency dispersion of the capacitance for this solar cell at a bias of V=0 volts. It is clear from the increase in capacitance at low frequencies ($\nu \leq 10$ Hz) that the depletion region of this cell is characterized by large numbers of defects with slow response times. This system is being developed as part of the M.S. thesis work of Fanning Shen who is using it for studies of the effects of different processing conditions and relating these to PL measurements on the same materials and devices.

Fig. 3.2 Dark and illuminated C-V characteristics of an rf sputtered CdS/CdTe solar cell (SSC 156). a) C vs. V plot; b) $1/C^2$ vs. V plot.

Fig. 3.3 Frequency dispersion of capacitance of CdS/CdTe solar cell #156.

4.0 Summer 1994 NSF Research Experiences for Undergraduates projects

As in the past two summers, we have involved undergraduate students in photovoltaics research as part of the National Science Foundation-sponsored Research Experiences for Undergraduates program at The University of Toledo. During the summer of 1994 four promising undergraduate students worked on activities related to this NREL contract. The four students were Paul Voyles from Oberlin College, Miranda Pearce from Reed College, David Spry from the University of Toledo, and Ed DesPlaines from the University of Connecticut. Their projects are briefly described below.

1. *Paul Voyles from Oberlin College in Oberlin, OH: "Copper-doped ZnTe as a back contact for CdTe solar cells."* This was designed as an initial study of the possible use of Cu-doped ZnTe for contacts to CdTe. Although the final goal would be to use sputtered films, Paul prepared his films and cells using laser deposition because he could prepare his own copper-doped targets in a range of concentrations. He measured the conductivity of films grown on glass using a strip line geometry. His results show a sudden increase in conductivity by about seven orders of magnitude for copper concentrations between 0.5% and 1% by weight in the target. (See Fig. 4.1) Paul found that for contact to the Cu-doped ZnTe films, pure gold made a very good, ohmic contact. He determined the stability of the copper-doped ZnTe films under CdCl_2 treatments and air anneal. Surprisingly he found that the CdCl_2 treatment + 400 C anneal of copper-doped films gave poor results. All of the ZnTe:Cu films became discolored and discontinuous although the ZnTe films without Cu doping were stable. Consequently, when he tested the ZnTe:Cu for contacts on solar cells, he did the ZnTe application after the CdCl_2 treatment was complete. He prepared two test solar cells by depositing ZnTe on top of $\text{SnO}_2/\text{CdS}/\text{CdTe}$ structures; however, the results showed evidence of back-to-back junctions which we believe is unrelated to the use of ZnTe:Cu. His work is being continued by other students.

Fig. 4.1: Resistivity of copper-doped ZnTe films grown by LPVD. Horizontal axis is the mass fraction of Cu in the target. Curve is drawn to guide the eye.

2. *Miranda Pearce from Reed College in Portland, Oregon: "The Use of CdZnTe to Create a Graded Band Gap in II-VI Semiconductor Heterojunction Solar Cells."* Miranda also used laser deposition because of the flexibility in preparing several different targets of the alloy CdZnTe with different Zn ratios. She grew six Cd_{1-x}Zn_xTe films at substrate temperatures between 200 and 400 C. 365 C was chosen as a good growth temperature. Then she grew six additional films from target concentrations between 2% and 50% Zn. With help from graduate students, Miranda used optical absorption, Raman scattering, x-ray diffraction, and EDS to identify the Zn concentration in the as-grown films. (This did not always match the target concentration.) As an example, Figure 4.2 shows the <111> diffraction peak from five films of different Zn concentration. Finally four complete cells were fabricated using the x=0.15 target with a cell efficiency of 6% achieved from a 15% CdZnTe layer as the absorber. (See Fig. 4.3.) We feel these results are promising as a first step toward the eventual use of a graded band gap absorber material.

Fig. 4.2: Peak position of the <111> x-ray reflection for several Cd_{1-x}Zn_xTe films. For the samples CZT10,9,8,5, and 12 respectively, the target concentrations were x = 0.20, 0.07, 0.15, 0.33, and 0.50.

Fig. 4.3: I-V curve for a glass/SnO₂/CdS/Cd_{0.85}Zn_{0.15}Te/Cu/Au solar cell fabricated by LPVD. $V_{oc}=0.677$, $J_{sc}=15.18$ mA/cm², FF=0.614, AM1.5 η =6.3%

3. *David Spry from the University of Toledo: "Oxygen Doped Polycrystalline Thin Film Cadmium Telluride."* David worked with Prof. Bohn and with graduate student Andreas Fischer to study the influence of oxygen on the growth of CdTe by laser deposition. David used a strip-line geometry for the resistivity measurements because all of the samples were highly resistive. Andreas prepared a number of CdTe films with partial pressures of O₂ of <0.1 mT, 1 mT and 5 mT in the laser deposition chamber, substrate temperatures from 350 to 400 C, and laser pulse energies from 70 to 130 mJ. Using resistivity as the criterion, the optimum O₂ pressure was 1 mT, optimum laser power was 90 ± 10 mJ, with no strong dependence on substrate temperature between 350 and 400 C. Fig. 4.4 shows the dependence of CdTe resistivity on laser pulse energy for films grown in 1 mT of O₂. Growth in O₂ at 1 mT reduced the CdTe film light resistivity (AM1.5) from $\sim 1 \times 10^7$ Ω -cm to $\sim 1 \times 10^6$ Ω -cm, although films grown in vacuum were reduced in conductivity also by about a factor of ten when annealed in air at 385 C for 20 min (without the use of any CdCl₂ treatment). Air anneal did not further reduce the resistivity of films grown in 1 mT of O₂. David obtained temperature dependences of the conductivity for most of the films and obtained activation energies as well. This work is now being completed on the last several samples. We hope soon to examine the effect of small amounts of oxygen in rf sputter deposition as well as for these laser-deposited films.

4. *Edward DesPlaines from the University of Connecticut: "C-V Measurements of CdTe Solar Cells."* Ed worked under the direction of Prof. Rajakarunanayake and graduate student Faming Shen to set up a C-V measurement system for solar cells. The system was described in Section 4 above. Ed used this system to obtain some measurements on a cell from Solar Cells Inc, and several cells from our group. Faming Shen has used this system to study a $\sim 10\%$ efficient cell grown by rf sputtering. His results were described above in Figures 3.2 and 3.3.

Fig. 4.4: In-plane resistivity under AM1.5 conditions at 290K for LPVD CdTe films grown at 370 C and 1 mTorr O₂ pressure vs. laser pulse energy; □ - as grown films, ■ - annealed in air at 400 C for 20 minutes.

Research Apprenticeship in Science Program (RASP)--In addition to the undergraduate students, a Toledo high school student, Michelle Cimini, worked on a research project in our laboratory. Michelle was a participant in the U. of Toledo-sponsored program RASP. She studied principally the effects of doping aqueous solutions of graphite (Aquadag) with CuCl₂ and with HgTe. She studied dopings of 1, 2, 5, and 10% CuCl₂ by weight and 0.5, 1, 2, and 5% HgTe by weight. After anneals at 150 C or 200 C in air, the best open circuit voltages were 0.79 V for 0 to 2% CuCl₂. Higher CuCl₂ dopings gave poorer voltages. Doping with HgTe powder gave little change in open circuit voltages up to the 5% doping studied. Apparently the HgTe was not very active at the annealing temperatures of 150 - 200 C.

We expect to continue our involvement with summer undergraduate students through the NSF-REU program and also with an occasional high school student. We have found that there are many photovoltaics-related projects which can be quite stimulating to college and high school students. With careful oversight and management, these projects can yield benefits for the ongoing research program as well.

5.0 Conclusions

During the past year we have begun using a new sputter deposition chamber which we designed to accommodate two 2-inch diameter rf magnetron guns with maximum possible isolation--i.e., they are mounted in opposite arms of a six-way cross with eight inch diameter ports. The system includes small 45° optical access ports which has permitted us to use an optical reflection interference method for non-contact glass substrate temperature measurements and optical transmission measurements for real time film thickness measurements. These real time, *in situ* monitors have saved a considerable amount of time and effort in the process of cell fabrication.

The two magnetrons initially installed in this system were obtained from different manufacturers (AJA International and Kurt J. Lesker Co.). The guns, as acquired, were set up with quite distinctive magnetic field configurations and different field strengths as well. We invested considerable effort into characterizing the differences in the rf plasmas from the two guns. Our measurements included optical emission spectroscopy, Langmuir probe measurements, as well as target self-bias measurements and growth rate measurements. In addition, we have examined the dependence on sputter gun of: 1) the film morphology via SEM studies, 2) the lattice constant via x-ray diffraction, 3) the photoluminescence efficiency. The completed solar cells were tested with I-V measurements, C-V measurements, and examined with SEM, and photoluminescence techniques.

We have found that the magnetron magnetic field strength and configuration as well as substrate temperature, sputter gas pressure, and substrate bias all have considerable effects on the materials quality and on the performance of the solar cells. At this point, the unbalanced magnetron appears to produce the better film quality as measured by photoluminescence, SEM, and the cell performance. We believe that the magnetic field differences between guns as well as the effects of gas pressure and substrate bias are affecting the details of the ion, and possibly electron, bombardment of the growing films. Our understanding of these effects is far from complete, but we believe that understanding and optimizing these parameters will be key to further improvements in the performance of rf sputtered CdS/CdTe solar cells.

During this year, we have begun a series of studies of ternary alloys. Films of CdZnTe were deposited by LPVD and the deposition conditions approximately optimized. A small number of cells were fabricated with the CdTe replaced by CdZnTe to further test the electronic quality of the films. A cell efficiency of 6.3% was obtained for 15% Zn concentration without serious optimization.

6.0 Future Directions

The strong dependence of the sputtered film quality on the magnetic field strength and configuration of the magnetrons came as somewhat of a surprise to us and we are now working to further elucidate the underlying causes of this behavior. Thus we have acquired a second magnetron gun of the unbalanced type and are presently producing films and cells with two unbalanced magnetic field guns mounted in the chamber. However, we expect that the optimum film quality, especially the electrical characteristics, may require further adjustment of the strength and/or configuration of the magnetron magnetic field. In addition, we need to determine whether any possible effects arise from the stray magnetic fields of the second gun.

A second important result of our studies is the ability to control to some extent the degree of strain in the films by adjusting the sputter gas pressure. In addition, it is possible that control of magnetic fields may also affect the strain in the as-grown films. These aspects are being investigated during the second contract year. In parallel studies, we shall continue efforts on optimizing the preparation of ternary alloy films of, e.g., CdZnTe and CdZnS and incorporate these into solar cells as replacement layers for the CdTe and CdS respectively and also as graded

layers. This work will be done initially with LPVD and then be extended to the use of rf sputtering.

We are working to improve our capabilities for low temperature PL studies. We are designing a fiber-optic system to allow small samples to be immersed in a liquid helium storage dewar with the laser light and PL light to be coupled into and out of the sample with optical fibers. This should provide excellent thermal cooling of films on glass substrates, provide cooling down to 4.2 K, and obviate the need for an optical access research cryostat. The system will also incorporate the use of laser diodes for resonant excitation of CdTe Raman and PL signals.²⁰

7.0 Acknowledgments

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M.S. August 1994

"Electrical and Morphological Properties of Polycrystalline CdS Thin Films"

Fanning Shen

M.S. in progress

"Capacitance-Voltage Measurements on CdS/CdTe Solar Cells"

Chitra Narayanswami

M.S. in progress

Zhirong Feng

M.S. June 1994

"Photoreflectance and Electoreflectance Studies of CdTe Films and CdTe/CdS Heterostructures"

Ph.D. in progress

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Ph.D. June 1995

"CdTe and CdS Thin Film Preparation Using RF Planar Magnetron Sputtering"

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Ph.D. in progress

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13. ABSTRACT (Maximum 200 words) This report describes work performed to develop and optimize the process of radio frequency (RF) sputtering for the fabrication of thin-film solar cells on glass. The emphasis is on CdTe-related materials including CdTe, CdS, ZnTe, and ternary alloy semiconductors. Pulsed laser physical vapor deposition (LPVD) was used for exploratory work on these materials, especially where alloying or doping are involved, and for the deposition of cadmium chloride layers. For the sputtering work, a two-gun sputtering chamber was implemented, with optical access for monitoring temperature and growth rate. We studied the optical and electrical properties of the plasmas produced by two different kinds of planar magnetron sputter guns with different magnetic field configurations and strengths. Using LPVD, we studied alloy semiconductors such as CdZnTe and heavily doped semiconductors such as ZnTe:Cu for possible incorporation into graded band gap CdTe-based photovoltaic devices.					
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