Radio-frequency-magnetron-sputtered CdS/CdTe solar cells on soda-lime glass

M. Shao, A. Fischer, D. Grecu, U. Jayamaha, E. Bykov, G. Contreras-Puente,[a)]
R. G. Bohn, and A. D. Compaan[b)]
Department of Physics and Astronomy and Center for Materials Science and Engineering, The University of Toledo, Toledo, Ohio 43606

(Received 23 July 1996; accepted for publication 4 September 1996)

We report the fabrication of an 11.6% efficient, polycrystalline thin-film CdS/CdTe solar cell in which both semiconductor layers were deposited by planar-magnetron-radio-frequency sputtering at 380 °C on commercially available soda-lime float-glass substrates coated with SnO_2:F. We show that the magnetron magnetic field is critical to obtaining high cell efficiency. Much stronger photoluminescence and higher electrical conductivity are found in films and cells grown with unbalanced-field magnetrons. The magnetic field dependence is interpreted as arising from the enhanced electron and ion bombardment of the film growth interface when unbalanced magnetrons are used. © *1996 American Institute of Physics.* [S0003-6951(96)02546-6]

For polycrystalline thin-film solar cells on glass it is critical to obtain the highest possible film quality at low growth temperatures. In the case of solar cells, high film quality includes not only the elements of density, morphology, and strain, but more importantly, superior electrical performance including long minority carrier lifetimes. The highest reported efficiency for CdS/CdTe solar cells, 15.8%, was obtained using borosilicate glass substrates with film deposition by closed-space sublimation[1] and a substrate temperature of 625 °C, which is too high for the soda-lime glass substrates desired for large-area solar modules. The enhanced adatom mobility at the growth interface, which is achieved with elevated growth temperature, may also be obtained by supplying nonthermal energy to the growth interface. One method for supplying this additional energy over a large-area growth surface is through the use of energetic electrons, atoms, and/or ions.

Planar magnetron sputtering[2] can be designed to supply these energetic particles and, furthermore, sputtering is readily scalable to large areas. In this letter we show that ion and electron bombardment, which is readily controlled by the magnetic field of the planar magnetron sputtering source, can have pronounced effects on the minority carrier lifetime as evidenced by the photoluminescence (PL) efficiency and spectra of the individual CdS and CdTe films. Not surprisingly, the performances of the resulting solar cells are also strongly affected by the magnetic field configuration, with efficiencies ranging from 2% for a balanced magnetron to 11.6% for a strongly unbalanced magnetron.

One of the first definitive studies of the effects of magnetic field configuration in magnetron sputtering was presented by Window and Savvides.[3] Their work focused on the microstructure, strain, and surface morphology of metal films. Greene and collaborators[4] have examined magnetic field effects on mechanical properties of films such as TiN. A recent review of unbalanced magnetron sputtering has been given by Rohde.[5] Although some work has been directed to the examination of changes in electrical resistivity of magnetron-sputtered Cu films, few studies have focused on the photoelectronic properties of magnetron-sputtered semiconductor films and their dependence on the magnetic field configuration.

A ''balanced'' field magnetron has essentially all field lines completed in the half-plane above the sputtering target, forming a magnetic trap just above the target. We have used a magnetron from Lesker[6] with the balanced magnetic field as sketched in Fig. 1(a). Alternatively, with different placement of permanent magnets in the sputtering gun or with suitable external field coils, it is possible to obtain a ''type I'' or a ''type II'' unbalanced magnetron. For the type II unbalanced magnetron, we have used a gun from AJA

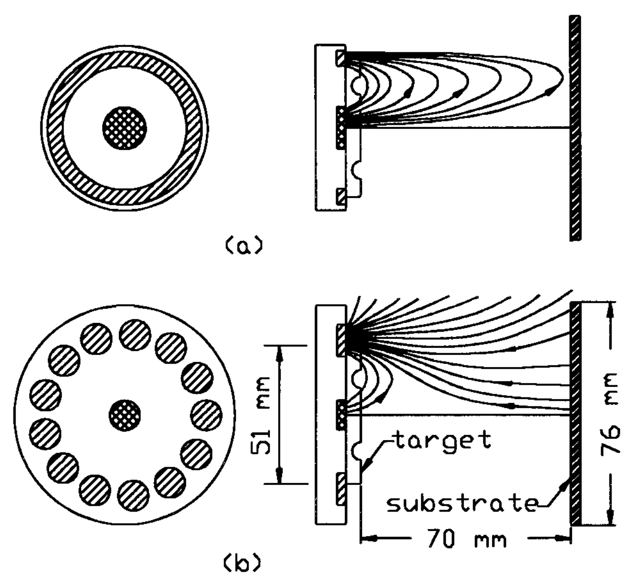

FIG. 1. Top and side views of the two planar magnetron sputter guns showing magnet placement, target, and substrate location, and magnetic field lines based on measurements by a Hall-effect gaussmeter. (a) Balanced gun with annular ring magnet; (b) type II unbalanced gun with ring of magnets.

[a)]On sabbatical leave from E.S.F.M.-I.P.N., 07738 Mexico D.F.
[b)]Electronic mail: office@physics.utoledo.edu

TABLE I. Magnetron plasma characteristics (P_{rf}=25 W, p_{Ar}=18 mT, CdS target.

Parameter	Unbalanced	Balanced
Substrate self-bias, V_{sb}	−2.2 V	+8 V
Plasma potential, V_p	+25 V	+29 V
Substrate sheath, $V_p - V_{sb}$	+27 V	+21 V
Ion flux, F_I(cm^{-2} s^{-1})	1.8×10^{15}	1.0×10^{15}
Deposition flux, F_{Cd+S}(cm^{-2} s^{-1})	2.4×10^{15}	2.6×10^{15}
F_I/F_{Cd+S}	0.75	0.4
Electron temperature, T_e	5.3 eV	4.0 eV
Electron density, n_e (cm^{-3})	7.6×10^{10}	3.9×10^{10}

International[7] with the field as sketched in Fig. 1(b). For a type II unbalanced gun, the magnetic field at large distance is dominated by the outer ring of magnets and the field lines form a type of ''chimney'' acting on the electrons produced at or near the sputtering target and directing onto an opposed substrate many of those that escape the magnetic trap. Since the plasma tends to remain neutral, the additional flux of electrons will ''pull'' a corresponding flux of positive ions along. By contrast, the field of a type I magnetron is dominated by the strong central magnet and has field lines that direct electrons away from an opposed deposition substrate toward the walls of the sputtering chamber. In the unbalanced magnetrons, the field lines are not closed in the upper half-plane but are completed through the side and back walls of the sputtering gun. Further descriptions of these magnetic field configurations are given in Ref. 3.

As discussed below, we find that there are significant differences in the plasma characteristics of the two guns used for this work and in the ion fluxes incident on the growth interface. (In addition to the differences in field *configuration*, the nearly balanced field gun that we have used has weaker field *strength* near the target, ~50 G versus ~600 G for the unbalanced gun.) These differences have profound effects on the electronic quality of the rf sputtered films of CdS and CdTe as observed by photoluminescence and in the solar cell performance.

The CdS and CdTe films were deposited in a specially constructed, turbopumped rf sputtering chamber built from a six-way stainless cross.[8] Magnetrons accommodating 50 mm diam targets were mounted in opposing arms of the cross. The substrate was radiatively heated with a tantalum wire serpentine heater.[9] The mounting assembly was electrically isolated so that electrical bias could be applied during deposition, although no substrate bias was used in the results reported here. The sputter target-substrate distance was 70 mm.

We have measured the properties of the rf plasma using a Langmuir probe (0.1 mm×5 mm tantalum wire) extended from a glass capillary located parallel to and 1 cm in front of the substrate.[8,10] Analyses of the $I-V$ behavior of this probe yield approximate values for the plasma density, electron temperature, and plasma potential during film growth. A summary of the plasma characteristics is given in Table I, for an Ar pressure of 18 mTorr, rf power of 25 W, and a CdS target. From the self-bias potential of the electrically floating, tin–oxide coated glass substrate, we can estimate the substrate sheath potential that establishes the typical ion impact energy on the growth interface (27 and 21 V, respectively, for the unbalanced and balanced guns). Table I shows that the electron temperature at the probe is higher for the unbalanced magnetron. The substrate sheath potential (ion energy) is slightly higher, and the ion flux on the substrate is almost a factor of 2 higher for the unbalanced magnetron. From the film growth rate we can estimate the ratio of ion flux to deposition flux (Cd+S). This ratio approaches unity for the unbalanced gun.

The effect of magnetron magnetic field showed up clearly in photoluminescence of individual films of CdTe where we found that films grown with the unbalanced magnetron had PL stronger by about 10^3. These PL data point to the improved minority-carrier lifetime in the films grown with the unbalanced magnetron. In addition, the electrical conductivity of CdTe films grown with the unbalanced magnetron was 10–100 times higher than for films grown with the balanced gun, in both dark and one-sun conditions.

For our solar cells,[11] we used substrates of soda-lime glass coated with SnO_2:F (LOF 10 Ω/□).[12] Film thicknesses (0.25 μm CdS and 2.0 μm CdTe) were determined and controlled with an *in situ* measurement of optical absorption as described earlier.[8,9] To complete the cell fabrication, we deposited ~0.2 μm of $CdCl_2$ by pulsed laser ablation and then annealed the cells in air at 400 °C for 20 min followed by a deionized water rinse. We used evaporated Cu (4 nm) and Au (20 nm) for the back contact followed by a 30 min diffusion step at 150 °C. No chemical etches or hydrogen treatments were used in the fabrication process.[9,11]

Using two unbalanced magnetrons and one balanced magnetron, we fabricated cells with the three possible combinations of guns for the CdS and CdTe layers while keeping other process conditions the same. In this series, we found highest efficiency (~11.4%) when both layers were deposited with unbalanced guns and lowest efficiency (~2%) when the balanced gun was used for the CdTe layer. For

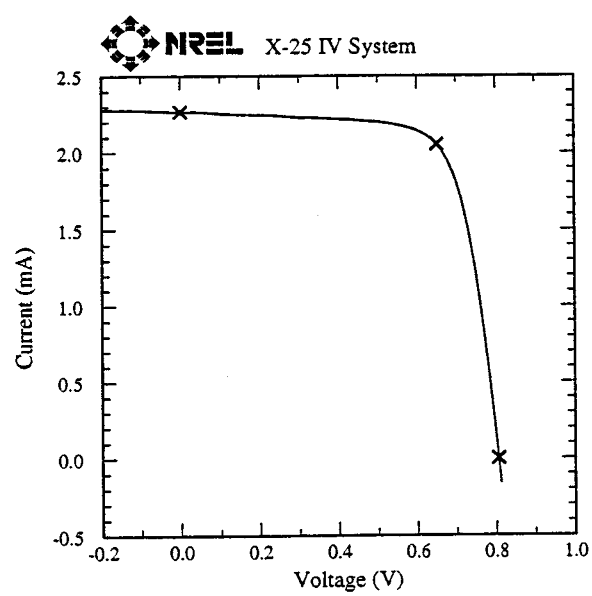

FIG. 2. $I-V$ response of all-sputtered cell measured at NREL (area=0.115 cm^2, temp=25 °C, irradiance 1000 W/m^2, V_{OC}=806 mV, J_{SC}=19.7 mA/cm^2, fill factor=73.3%, η=11.6%).

balanced-gun deposition of the CdS layer the efficiency was ~10.3%. The performance differences are consistent with the understanding that virtually all of the current in CdS/CdTe solar cells, including these rf sputtered cells, is produced from electron-hole pair generation in the CdTe layer.

The National Renewable Energy Laboratory (NREL) efficiency test of one of our all-sputtered cells is shown in Fig. 2. Their quantum efficiency test, not shown here, indicates that absorption in the 250 nm CdS window layer is responsible for poor response in the region below $\lambda=500$ nm. Reduction of this CdS thickness could yield an additional 3 mA/cm^2 of current density,[13] however, we have not yet been successful with thinner CdS layers on this commercial SnO_2-coated soda-lime glass. Our evaporated Cu/Au back contact is not fully stable, and from our measurements before and after the NREL tests, we estimate that the one-sun efficiency degraded by about 0.5% absolute over the ~1 month before the data of Fig. 2 were taken. Other groups have shown that different contacting schemes for CdS/CdTe cells can yield stable performance[1,14] although we have not yet optimized these schemes for our all-sputtered cells. However, we believe that >13% AM 1.5 efficiency cells, and high efficiency modules should be achievable by unbalanced planar magnetron rf sputtering.

The authors gratefully acknowledge the financial support of the National Renewable Energy Laboratory. The authors are also indebted to Halden Field of NREL for the cell performance measurements. In addition, Chad Tabory (deceased), Zhirong Feng, and Stacy Nance helped in many ways with film characterization, measurements of cell performance, and in many aspects of the cell fabrication.

[1] C. Ferekides, J. Britt, Y. Ma, and L. Killian, *Proceedings of the 23rd IEEE Photovoltaic Specialists Conference—1993)* (IEEE, Piscataway, NJ, 1993), pp. 389–393; T. L. Chu, S. S. Chu, J. Britt, C. Ferekides, C. Wang, C. Q. Wu, and H. S. Ullal, IEEE Electron Device Lett. **13**, 303 (1992).
[2] A. D. Compaan, C. N. Tabory, Y. Li, Z. Feng, and A. Fischer, *23rd IEEE Photovoltaic Specialists Conference—1993* (IEEE, Piscataway, NJ, 1993), pp. 394–399; M. Shao, U. Jayamaha, E. Bykov, C. N. Tabory, and A. D. Compaan, *25th IEEE Photovoltaic Specialists Conference—1996* (IEEE, Piscataway, NJ) (to be published).
[3] B. Window and N. Savvides, J. Vac. Sci. Technol. A **4**, 196 (1986).
[4] I. Petrov, F. Adibi, J. E. Greene, W. D. Sproul, and W.-D. Munz, J. Vac. Sci. Technol. A. **10**, 3283 (1992); F. Adibi, I. Petrov, J. E. Greene, U. Wahlstrom, and J.-E. Sundgren, J. Vac. Sci. Technol. A. **11**, 136 (1993).
[5] Suzanne L. Rohde, in *Plasma Sources for Thin Film Deposition and Etching*, edited by M. H. Francombe and J. L. Vossen (Academic, New York, 1994), pp. 235–288.
[6] K. J. Lesker, 1515 Worthington Ave., Clairton, PA 15025.
[7] AJA International, P.O. Box 246, North Scituate, MA 02060.
[8] A. D. Compaan, M. Shao, C. N. Tabory, Z. Feng, A. Fischer, I. Matulionis, and R. G. Bohn, *Proceedings of the 24th IEEE Photovoltaic Specialists Conference—1994* (IEEE, Piscataway, NJ, 1995), pp. 111–114; A. D. Compaan, M. Shao, C. N. Tabory, Z. Feng, A. Fischer, F. Shen, C. Narayanswami, and R. G. Bohn, in *13th NREL Photovoltaics Program Review*, Conf. Proc. No. 353 edited by H. S. Ullal and C. E. Witt, AIP (AIP, Woodbury, New York, 1995), pp. 360–367.
[9] Z. Feng, C. N. Tabory, and A. D. Compaan, *Proceedings of the 24th IEEE Photovoltaic Specialists Conference—1994* (IEEE, Piscataway, New Jersey, 1995), pp. 350–353.
[10] Meilun Shao, Ph.D. thesis, University of Toledo, 1995 (unpublished).
[11] A. D. Compaan, U.S. Patent No. 5,393,675 (Feb. 28, 1995).
[12] Libbey-Owens-Ford, P.O. Box 799, Toledo, OH, 43695.
[13] J. E. Granata, J. R. Sites, G. Contreras-Puente, and A. D. Compaan, *25th IEEE Photovoltaic Specialists Conference—1996* (IEEE, Piscataway, NJ, to be published).
[14] B. Kroposki, T. Strand, R. Hansen, R. Powell, and R. Sasala, *25th IEEE Photovoltaic Specialists Conference—1996* (IEEE, Piscataway, NJ, to be published).