

# THE ROLE OF OXYGEN IN CdS/CdTe SOLAR CELLS DEPOSITED BY CLOSE-SPACED SUBLIMATION

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## ABSTRACT

The presence of oxygen during close-spaced sublimation (CSS) of CdTe has been previously reported to be essential for high-efficiency CdS/CdTe solar cells because it increases the acceptor density in the absorber. We find that the presence of oxygen during CSS increases the nucleation site density of CdTe, thus decreasing pinhole density and grain size. Photoluminescence showed that oxygen decreases material quality in the bulk of the CdTe film, but positively impacts the critical CdS/CdTe interface. Through device characterization we were unable to verify an increase in acceptor density with increased oxygen. These results, along with the achievement of high-efficiency cells (13% AM1.5) without the use of oxygen, led us to conclude that the use of oxygen during CSS deposition of CdTe can be useful but is not essential.

## INTRODUCTION

CdS/CdTe solar cells are notable contenders in the race for inexpensive, high-efficiency photovoltaics [1]. The breakthrough that created much of the current interest in n-CdS/p-CdTe thin-film cells was the use of oxygen ambient during close-spaced sublimation (CSS) of CdTe by researchers at Eastman Kodak. Through this innovation, they were able to break the 10% efficiency barrier for thin-film CdTe solar cells [2]. The use of oxygen during CSS deposition of CdTe culminated at the University of South Florida with a 15.8% cell, the current world record for CdTe cells [3,4].

To date, research on oxygen ambient has focused on its effect as a dopant. It has been reported that oxygen is essential to high-efficiency cells because it increases the acceptor density in the CdTe absorber, thus preventing deeply-buried homojunction formation [5-8]. Deeply-buried junctions have low photon collection due to the high absorption coefficient of CdTe.

The presence of oxygen during deposition has some disadvantages. Depositions in an oxygen ambient cause CdTe sources to non-uniformly oxidize, reducing the source flux [9]. Additionally, oxygen can cause surface features of 0.5 to 10  $\mu\text{m}$  in height on the CdTe film, most likely through ejection of particles from the source material [9]. These effects can reduce device efficiency and run-to-run reproducibility, which could present problems for high-volume manufacturing.

Because the use of oxygen has disadvantages, we were led to the questions, "What is role of oxygen in CSS CdTe cells, and is it truly essential?" In this paper we describe some effects of oxygen other than doping. We also report high-efficiency CdS/CdTe solar cells made without oxygen in any stage of production and present a plausible alternative to the theory that oxygen acts as an acceptor in CSS-deposited CdTe.

## EXPERIMENTAL DESCRIPTION

Solar cells were fabricated with a superstrate structure consisting, in most cases, of the following layers: glass/SnO<sub>2</sub>/CdS/CdTe/back contact material (HgTe:Cu-doped graphite or multilayer metal). The substrate used for the majority of experiments was Corning 7059 glass, with a SnO<sub>2</sub> layer (Solarex) serving as the transparent front contact. A thin (600-1200 Å) CdS layer was applied by chemical bath deposition [9] and then annealed at 400°C in 30 torr H<sub>2</sub> for 15 minutes. CSS deposition of the CdTe was accomplished by placing a CdTe source plate in close proximity (2-6 mm) to the substrate. The source was heated to 630°-680°C and the substrate to 500°-620°C. This arrangement causes Cd and Te to sublime from the source and diffuse to the substrate. The ambient used during CdTe deposition was a mixture of O<sub>2</sub> and He, with O<sub>2</sub> partial pressures of 0-24 torr and He partial pressures of 0-45 torr.

A post-deposition anneal was performed on most of the samples by soaking in CdCl<sub>2</sub> dissolved in MeOH, then annealing at 400°C for 40 minutes in a He or a He+O<sub>2</sub> ambient. A back contact was then applied. Additional details of processing CdS/CdTe cells by this method can be found in other publications [9].

Source and substrate temperature control for the CdTe deposition was accomplished by heating graphite susceptors with quartz-halogen lamps. We have previously reported that the graphite susceptors that have typically been used for CSS deposition (Poco Graphite DFP-3-2) can react with oxygen in the deposition chamber at a high enough rate to convert a large portion of the oxygen to CO and CO<sub>2</sub> [9]. The rate of reaction depends on the condition of the graphite susceptors and can change with use. The graphite susceptors used in the experiments for this paper had a pyrolytic graphite coating (Fabmate® from Poco Graphite) that reduced the reaction of the ambient oxygen with the susceptors to a negligible amount, thus providing a constant and reproducible ambient.

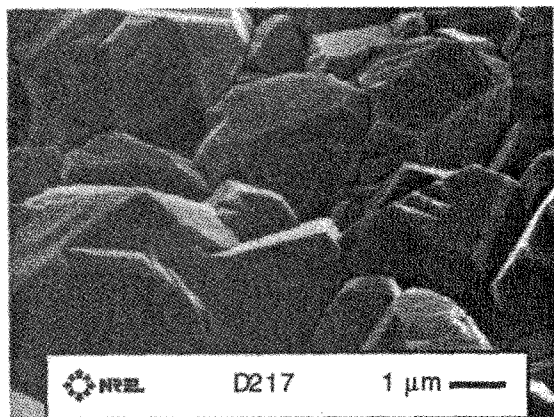
## RESULTS

### Nucleation and Growth

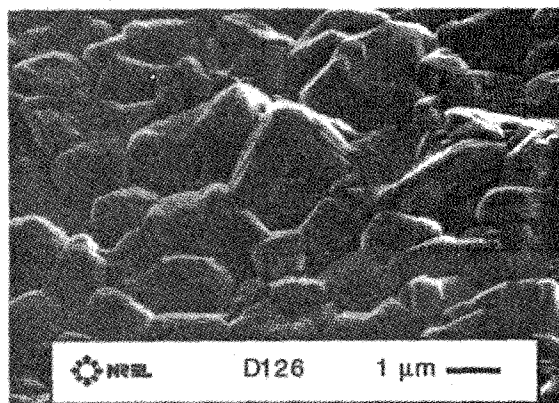
We determined that oxygen increases CdTe nucleation site density, based on the following evidence:

1. Decreased grain size and reduced faceting of CdTe films grown on CdS with oxygen ambient.
2. Improved CdTe coverage of bare glass and SnO<sub>2</sub> substrates with oxygen ambient.
3. Decreased pinhole density of CdTe films grown on CdS in oxygen ambient or on oxidized CdS films.

Grain size tends to scale with film thickness, and the presence of oxygen decreases the sublimation rate from the source; therefore, it was necessary to adjust deposition parameters to achieve similar film thicknesses to legitimately determine the effect of oxygen on grain size and faceting. Figures 1a and 1b are scanning electron micrographs of two films grown using deposition time to achieve similar CdTe thicknesses. The film grown in oxygen clearly has smaller, less-faceted grains.



**Fig. 1a.** CdTe film grown in 15 torr He (source = 640°C, substrate = 600°C, separation = 2 mm, deposition time = 1 minute; film is 4.3 μm thick).



**Fig. 1b.** CdTe film grown in 2 torr O<sub>2</sub> and 13 torr He (source = 640°C, substrate = 600°C, separation = 2 mm, deposition time = 5 minutes; film is 4.8 μm thick).

The trend of smaller, less-faceted grains with increasing O<sub>2</sub> partial pressure during deposition also holds when the adjustment to achieve similar thickness is done with source temperature or with source/substrate separation.

The ability of oxygen to improve initiation of CdTe growth on bare glass and SnO<sub>2</sub>-coated glass is clear. At high substrate temperatures, attempts to deposit CdTe on bare borosilicate glass in the absence of oxygen result in incomplete coverage. To achieve full coverage without oxygen, the substrate temperature must be well below 500°C (low temperature also increases nucleation site density). We found that high levels of oxygen (greater than 4 torr) are capable of producing complete CdTe coverage on bare glass at 600°C. The improvement of nucleation with oxygen is not as dramatic on SnO<sub>2</sub> as it is on bare glass, but it is still evident.

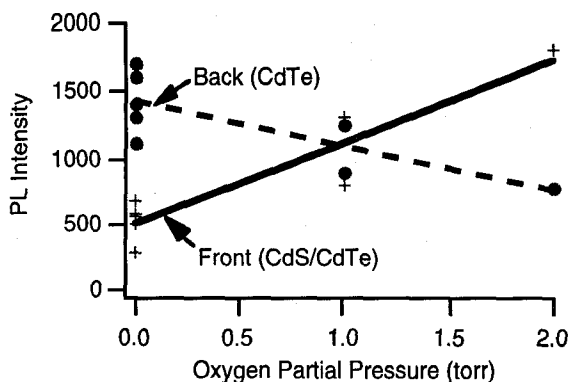
The tendency of oxygen to suppress pinholes can be witnessed by backlighting films with a strong, small light (e.g., a fiber-optic light source). We found that films grown on CdS in the absence of oxygen had to be very thick (10-20 μm) to prevent pinholes, whereas films grown in 0.5 to 2 torr oxygen could be free of pinholes at less than 3 μm.

We also found that oxidized CdS can suppress pinhole formation. A CdTe film was grown in the absence of oxygen on a CdS film that had been oxidized at 600°C in 1 torr oxygen for 20 seconds. This CdTe film had fewer pinholes than a film grown under similar circumstances without the prior oxidation of the CdS film. This result provides evidence that the effect of oxygen at the location of growth, and not changes in vapor constituents from source oxidation, is the cause of increased nucleation attributed to the presence of oxygen.

### Material Quality As Determined by PL

Through its effect on nucleation, grain size, and defect chemistry, oxygen ambient also affects the minority carrier lifetime in CdTe. We used time-resolved photoluminescence (PL) and PL spectroscopy to probe CdS/CdTe samples made at a range of oxygen partial pressures. Laser excitation at 600 nm allowed us to selectively probe within 1 μm of the surface from either the front (i.e., the CdS/CdTe side) or the back (i.e., the CdTe side) of the cell.

Our measurements indicate that, for as-deposited films, the bulk CdTe (near the back of the cell) is higher quality when growth takes place in the absence of oxygen, as evidenced by lower non-radiative recombination. We took the PL intensity (which indicates the radiative recombination) as a measure of material quality. Figure 2 shows the inverse relationship of the relative PL intensity for as-deposited bulk CdTe to the oxygen partial pressure during growth. In contrast, the intermixed CdS<sub>x</sub>Te<sub>1-x</sub> near the CdS/CdTe junction has improved quality with increasing oxygen. Figure 2 shows the direct relationship of the relative PL intensity from the CdS/CdTe interface to the oxygen partial pressure during growth.



**Fig. 2.** Relative PL intensity of as-deposited CdTe on CdS films. "Front" indicates illumination of the CdS/CdTe interface. "Back" indicates illumination of the CdTe side.

Like the as-deposited films, films treated by a CdCl<sub>2</sub> anneal showed decreased PL intensity with increasing O<sub>2</sub> for the bulk CdTe. For the CdS/CdTe side, a relationship between O<sub>2</sub> partial pressure and PL intensity after the CdCl<sub>2</sub> anneal was not evident; however, the PL intensity did increase to an average of 5000 (arbitrary units).

The peak wavelength of the photoluminescence also exhibited a dependence on oxygen partial pressure for as-deposited films. Increasing oxygen shifted the PL peak from 853 nm to 850 nm.

### Doping

Device characterization has not as yet corroborated the assertion, made in literature [5,7], that oxygen increases the acceptor density in CdTe. Our Capacitance-Voltage (CV) measurements have not shown a correlation between oxygen partial pressure during deposition and doping in the absorber. In addition, electron-beam-induced current (EBIC) and quantum efficiency (QE) measurements were not as conclusive regarding the correlation between the buried homojunction formation and reduced oxygen partial pressure as has been previously reported. Of the many cells that we have fabricated without oxygen, only a few exhibited the deeply buried junction phenomenon described in literature, as evidenced by a QE showing significantly lower collection of 650-nm light relative to the collection of 800-nm light.

EBIC line scans were performed on device cross-sections. Using peak collection to indicate junction location we have seen both shallow and deeply buried (> 1 μm) homojunctions in cells made without oxygen. Variation of junction depth from shallow to deep was also found within a given sample.

The most remarkable result concerning the doping effects of oxygen was the ability to make high-efficiency cells (13% AM1.5) without oxygen, thus countering the contention that oxygen during CSS deposition of CdTe is essential for high-efficiency cells. Many high-efficiency cells were made by depositing CdTe films in the absence of oxygen. These films were deposited to thicknesses of

15 μm to prevent pinholes, and the CdCl<sub>2</sub> anneal was done in a He ambient. There is, of course, the possibility that the previously reported benefit of increased acceptor density has been replaced in these cells by some unintended dopant.

CdTe is an efficient self-compensator, thus reducing the likelihood that low-level unintended dopants would have a large impact. Still, we performed several experiments to reduce the likelihood that an unintended dopant was present and was responsible for the shallow junction depositions despite the absence of oxygen.

The majority of high-efficiency, no-oxygen depositions were done using source plates of polycrystalline CdTe (99.999%, Johnson Matthey) on borosilicate glass or SnO<sub>2</sub>-coated glass. To reduce the possibility of benefits from the use of a source plate or unknown dopants in the CdTe source material, we made a cell using high-purity CdTe (99.99999%, Alfa Aesar) directly from sintered powder. This cell, after application of a MgF anti-reflection coating, had an AM1.5 efficiency of 13.0% (V<sub>oc</sub> of 0.799 V, J<sub>sc</sub> of 22.54 mA/cm<sup>2</sup>, FF of 70.84%), as verified by the National Renewable Energy Laboratory.

To determine if the CdCl<sub>2</sub> dip/anneal step was doping the absorber and preventing deep junction formation, we made a cell without the CdCl<sub>2</sub> dip/anneal step and without oxygen during deposition. This cell had an efficiency of more than 6% and a QE indicative of a shallow junction.

To determine if the HgTe:Cu-doped graphite back contact we normally use was doping the absorber and preventing deep junction formation, we made a cell with a back contact similar to that used in literature [7]. Using a 1:88:35 nitric acid / phosphoric acid / deionized water etch followed by a deionized water rinse, then room temperature sputter deposition of 0.6 μm Ni on a film deposited without oxygen produced a cell with an efficiency of 9.7%.

These results indicate that high-efficiency cells are possible without extrinsic doping of the absorber. The ability of CdTe to self-compensate and its tendency to grow slightly p-type under some growth conditions support this possibility.

### Interaction with Substrate

The characteristics of the CdS layer appear to have a large impact on the CdTe growth in the absence of oxygen. On some of the SnO<sub>2</sub>-coated glass substrates used in these experiments, we deposited a thin layer (500-3000 Å) of not-intentionally doped tin oxide by sputtering in an O<sub>2</sub>/Ar ambient. Historically, this layer is added to increase the open-circuit voltage (V<sub>oc</sub>), with one possible explanation of its value being that it introduces a finite resistance in any shunt paths (pinholes), thus reducing their degradation of V<sub>oc</sub>. Although our studies have shown this layer to have marginal effect (+ or -) on cells deposited with oxygen ambient, this layer has a stark detrimental effect on cells made without oxygen. CdTe films made using substrates with this "intrinsic" SnO<sub>2</sub> layer (thus, glass/SnO<sub>2</sub>/i-SnO<sub>2</sub>/CdS/CdTe) tend to have pinholes,

reduced adhesion to the substrate, and a higher CdS/CdTe defect density as evidenced by PL measurements. These films also tend to produce low-efficiency devices. One intriguing explanation could be a strong dependence of growth and interdiffusion characteristics for different CdS films, where those differences are caused by differences in CdS nucleation for different substrates.

We also found that oxidation of the CdS on these substrates prior to CdTe deposition not only decreased the pinhole density, but allowed cells with greater than 10% efficiency to be produced without oxygen during the CdTe deposition.

## DISCUSSION

The nucleation and growth effects described in this paper have profound implications for solar cells. Decreased grain size will tend to increase recombination in the bulk of the CdTe; however, this negative effect could be outweighed by the benefits of reduced pinhole density and better coverage with thin films. The effect of oxygen on growth also impacts the most critical region of the cell, the CdS/CdTe interface. This concept, that oxygen can benefit the CdS/CdTe interface while reducing the quality of the bulk CdTe, was corroborated by the PL measurements and substrate interaction effects described in this paper.

What remains a question is whether or not oxygen acts as a dopant in CSS CdTe. Oxygen has previously been shown to compensate donors in CdTe deposited by a variety of methods [9]. However, prior to the groundbreaking work at Kodak, oxygen was not known to act as an acceptor in CdTe. The conclusion that oxygen acted as an acceptor in CSS CdTe was based primarily on device characterization [5], principally EBIC, QE, and CV. More fundamental studies were less conclusive. PL investigation of CSS CdTe showed no additional shallow acceptor level when illumination was from the CdTe side of the device [8]. Characterization of films on bare glass showed a carrier concentration of less than  $3 \times 10^{12} \text{ cm}^{-3}$  with an oxygen concentration of  $10^{19}$ - $10^{20} \text{ cm}^{-3}$  [6].

The conclusion that oxygen was essential because it acts as an acceptor in CSS CdTe was thus based primarily on device results. The devices we produced for this paper exhibited very different characteristics. For our cells, oxygen was not essential for producing high-efficiency cells, but was still useful for its effect on nucleation.

From the above results it appears plausible that oxygen does not act as an acceptor in CdTe, but instead, as a reactive gas that can alter the deposition conditions in a favorable manner. Thus, if the desired conditions can be achieved by means other than oxygen, such as through control of the characteristics of the CdS, then high-efficiency cells might be achieved reproducibly without the disadvantages, such as irreproducibility and material waste from source oxidation, that oxygen ambient during growth presents for high-volume manufacture.

## CONCLUSION

We have described several effects of oxygen, most notably the benefits of improved nucleation and improved CdS/CdTe junction formation. We have also produced high-efficiency devices without oxygen and proposed that oxygen may not, in fact, act as acceptor in CSS CdTe. We will continue to study the effects of oxygen with the intent of developing fabrication techniques that can provide the benefits attributed to oxygen without the manufacturing problems associated with its use.

## ACKNOWLEDGMENTS

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## REFERENCES

1. K. Zweibel, *Intl. J. Solar Energy*, **12**, 1992, pp. 285-292.
2. Y.S. Tyan and E.A. Perez-Albuern, "Efficient Thin-Film CdS/CdTe Solar Cells," *Proceedings of the 16th IEEE Photovoltaic Specialists' Conference*, 1982, pp. 794-800.
3. J. Britt and C. Ferekides, *Appl. Phys. Lett.*, **62** (22), 31 May 1993, pp. 2851-2852.
4. T. Chu and S. Chu, *Final Letter Report*, EAT-3-13159-01-104149, Oct. 1993.
5. Y.S. Tyan, F. Vazan, and T.S. Barge, "Effect of Oxygen on Thin-Film CdS/CdTe Solar Cells," *Proceedings of the 17th IEEE Photovoltaic Specialists' Conference*, 1984, pp. 840-845.
6. M. Hsu, R. Jih, P. Lin, H. Ueng, Y. Hsu, and H. Hwang, "Oxygen Doping in Close-Spaced-Sublimed CdTe Thin Films for Photovoltaic Cells," *J. Appl. Phys.*, **59** 1986, pp. 3607-3609.
7. Y.S. Tyan, "Topics on Thin Film CdS/CdTe Solar Cells," *Solar Cells*, **23**, 1988, pp. 19-29.
8. C.W. Tang and F. Vazan, "Effect of Oxygen on the Photoluminescence of CdS/CdTe Thin Films," *J. Appl. Phys.*, **55** (10), 15 May 1984, pp. 3886-3888.
9. D.H. Rose, D.S. Albin, R.J. Matson, A.B. Swartzlander, X.S. Li, R.G. Dhere, S. Asher, F.S. Hasoon, and P. Sheldon, "Effects of Oxygen During Close-Spaced Sublimation of CdTe Solar Cells," To be published in *Proceedings of the Materials Research Society, Volume J*, April 8-12, 1996, and references therein.