

Polycrystalline Thin Film Device Degradation Studies

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ABSTRACT

Oxygen during vapor CdCl₂ (VCC) treatments significantly reduced resistive shunts observed in CdS/CdTe polycrystalline devices using thinner CdS layers during 100 °C, open-circuit, 1-sun accelerated stress testing. Cu oxidation resulting from the reduction of various trace oxides present in as-grown and VCC treated films is the proposed mechanism by which Cu diffusion, and subsequent shunts are controlled. Graphite paste layers between metallization and CdTe behave like diffusion barriers and similarly benefit device stability. Ni-based contacts form a protective Ni₂Te₃ intermetallic layer that reduces metal diffusion but degrades performance through increased series resistance.

1. Objectives

The objective of this work is to identify and provide solutions for device-level stability issues that can negatively impact polycrystalline thin film module reliability goals for 20-30 year lifetimes as specified in the DOE-EERE Solar Program Multi-Year Technical Plan for 2003-2007 and beyond.

2. Technical Approach

The scope of this project involves the maintenance and use of a reproducible close-spaced sublimation (CSS) based CdTe fabrication process linked with downstream performance and stability metrics through a relational database. Experiments typically involve varying key parameters associated with *how* devices are made, and subsequently studying the *impact* of these changes on performance and stability. For some experiments, software is used to design efficient, large sample size sets that yield linear regression stability models. These models are used to identify significant primary effects that have the greatest impact on stability. Smaller experiments, with an emphasis on device characterization, are then used to develop the *fundamental science* explaining these empirical observations.

3. Results and Accomplishments

Two separate studies are discussed in this paper. In the first study, a large orthogonal experiment (48 devices) was used to determine how stability was affected when the CdS and CdTe film thickness was varied between 60 to 100 nm and 8 to 11 microns respectively. This study also involved determining the effects of nitric-phosphoric (NP) acid as a pre-contact etch and oxygen as an additive to the VCC process. In

the second study, the use of graphite layers with Ag and Ni-based adhesive backcontact pastes was investigated. In both studies, stability was ascertained by making current density-voltage (JV) measurements periodically after stressing devices under 1-sun, open-circuit bias at 100°C.

3.1 Film Thickness and VCC Oxygen Effects

Linear regression models correlating performance and stability with film thickness, the use of NP etch, and the presence of oxygen during the VCC process were developed using JMP (SAS Institute) software. Models were determined for both unstressed and stressed (t=693 hrs) device performance open-circuit voltage (V_{oc}), current-density (J_{sc}), fill factor (FF), and efficiency (Eff). P-value statistics for testing the significance of regression coefficients for each regressor variable were performed.

Implications of processing on initial performance and stability resulting from these models are discussed in detail elsewhere.^{1,2} An interesting observation during this study concerned the effect of CdS layer thickness. Though the highest initial performance resulted from using the thinnest CdS layers, increased shunting during stress testing negatively impacted stability. This shunting mechanism occurred in conjunction with the more gradual decrease in V_{oc} and FF associated with increased recombination with stress seen in all devices. The use of oxygen during the VCC process had a dramatic effect on reducing the more catastrophic shunt-related mechanism. Figure 1 shows the % change in Eff measured for thick CdTe (11 microns) devices using the thinnest (60 nm) CdS layers, with (solid circles) and without (open circles) NP etch, and with (solid lines) and without (dashed lines) oxygen (100 torr) during the VCC process.

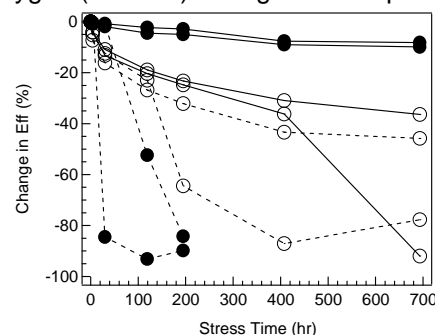


Fig. 1 Efficiency Degradation vs. Stress Time

In addition to the obvious benefit of oxygen, this figure also shows the subtle interaction between NP etch and oxygen where NP etched films require the

use of oxygen during the VCC process in order to be effective. Glancing angle x-ray diffraction (GIXRD) of device-representative CdTe film surfaces reveal the presence of various Te-oxide, and possibly cadmium tellurate and oxychloride phases resulting from the treatment of as-grown CdTe films in VCC processes containing oxygen. Though surface oxides are completely removed by NP etch, the presence of oxides along grain boundaries perpendicular to the film surface is suspected. A review of published thermodynamic data² concerning the reaction of CdTe with Cu, Cl and O suggests that oxidation of Cu dopant (the diffusion of which is known to be problematic), either by reduction of TeO₂ or other oxide phases present at grain boundaries is possible and may help reduce Cu diffusion in much the same way that Cu is "gettered" by Te in NP-etched devices³.

3.2 The Effect of Graphite Layers

The stability of CdTe devices made using four different back contact structures was studied⁴. These structures used either Ag or Ni-based organic pastes as the primary metallic conductor. In half of these devices, the Cu-doped graphite layer was left intact between the metal and the NP-etched CdTe surface during processing (graphite/Ag and graphite/Ni). In the remaining devices, the graphite layer was removed after the 280°C dopant drive step (Ag-only and Ni-only).

No measurable difference in performance or stability was observed among devices with the graphite layer present. The graphite in this case appears to behave like a diffusion barrier, possibly due to a cation exchange mechanism involving the polyacrylic acid (PAA) constituent of this paste. In the absence of graphite, devices showed much faster degradation.

Capacitance-voltage (CV) measurements were used to determine hole carrier concentration as a function of depletion width in unstressed and stressed (712 hrs) devices (Fig. 2).

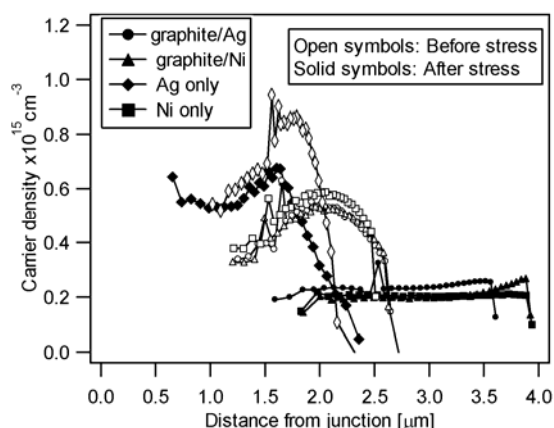


Fig. 2 CV profiles vs. Back Contact Structure

CV profiles before and after stress appear to behave identically with the sole exception of the Ag-only case.

The decreased carrier density and increased depletion width after stress observed in the graphite/Ni, graphite/Ag, and Ni-only devices is commonly observed in cells where Cu is depleted from the back contact⁵. The absence of this behavior in the Ag-only devices may be due to replenishment of Ag from the contact itself. Ag is known to be a rapid diffuser, as well as dopant in CdTe.

The rapid diffusion of Ag in CdTe, particularly at grain boundaries resulted in greater micro non-uniformity formation with stress for the Ag-only devices relative to other cells as determined by light beam induced current (LBIC) measurements. For Ni-only devices, Ni diffusion was minimized by the formation of a Ni₃Te₂ layer detected by GIXRD at the Ni-CdTe interface. Shunting was not observed in the Ni-only case (as it was for the Ag-only devices). However, the increased resistance of this layer contributed to increased series resistance.

4. Conclusions

Cu oxidation, graphite layer diffusion barriers, and intermetallic phase formation were used to explain improved stability observed within the context of two studies involving CdS/CdTe devices. Future work will focus on maintaining stability while reducing the thickness of CSS grown CdTe devices.

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