CONTINUOUS IN-LINE PROCESSING OF CdS/CdTe DEVICES: PROCESS CONTROL USING XRF AND EFFICIENT HEATING

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ABSTRACT

A simple, quick, and non-destructive way to measure deposited Cu, used for back contact formation, and thickness of CdS and CdTe layers in the device is desirable for manufacturing process control. A simple X-ray Fluorescence (XRF) system was investigated for these measurements. Experiments show that 5 min. polychromatic XRF spectra can be used to measure CdTe and CdS thickness, and accurate 30 sec. measurements are possible. Statistical integrity of Cu concentration measurements was investigated. XRF measurements are able to differentiate Cu concentrations within 10% of nominal, making it useful for process control. A description of a new, improved in-line R&D deposition system is also presented. Thermal modeling results show the new NiCr wire based heating system will reach desired operating temperatures while providing opportunities for improved temperature uniformity and energy usage.

INTRODUCTION

Low cost manufacturing and adequate stability has enabled CdS/CdTe solar cells to become a market leader in PV. A simple and non-destructive way to measure thickness of CdS and CdTe layers in the device is desirable for process control. Surface and interface roughness of the device complicate optical measurement methods, such as ellipsometry and reflectometry. A roughness independent thickness measurement technique can circumvent these problems. One such technique is thickness measurement using data from X-ray Fluorescence (XRF). X-rays of relatively high energy (30-40 keV) can be generated by a small X-ray tube and are weakly attenuated by 2-3 µm CdS/CdTe films. Incident X-rays absorbed in the film eject photoelectrons from inner orbitals of heavier atoms in the film. The resulting vacancies are filled by electrons from higher orbitals, which decay to the lower levels by isotropically emitting characteristic X-rays (e.g. 23.17 keV for Kα of Cd). An X-ray spectrometer placed in proximity to the sample will collect a number of weakly absorbed characteristic X-rays roughly proportional to the mass of the element present in the film.

Additionally, stability issues are encountered when excessive Cu is used for back contact formation [1]. Previously we have shown that optimum amounts of Cu are beneficial for back contact formation without negative stability effects in CdS/CdTe devices [2]. Controlling Cu levels during manufacturing is important for maintaining acceptable stability. Several time consuming and destructive characterization techniques can measure Cu levels, such as SIMS, but XRF can be an acceptable technique for process control of Cu in manufactured cells and has been used extensively in manufacturing of CIGS solar cells [3]. The advantage of using XRF is that the data can be gathered quickly, both thickness and Cu measurements can be done simultaneously, and it is non-destructive. The objective of this study is to explore use of XRF to measure CdTe and CdS thickness, develop a better model of this measurement, and to investigate the statistical integrity of Cu measurements in CdTe films prior to metallization.

We also present advances in more efficient heating of graphite sources. The original continuous in-line R&D system, as we have described earlier [4], was beneficial in demonstrating fast, large scale manufacturing. An advanced R&D system has been constructed to improve process flexibility and reduce experimentation time. Along with the new R&D system, new heating system was designed for the deposition source in order to improve temperature uniformity and energy usage. Heat transfer modeling results of this new heater design were used to evaluate the functionality of this design prior to construction. These results are also presented.

METHODS

Samples were made using the continuous in-line deposition system [4]. XRF analysis was performed with an Innov-X Systems Alpha Series XRF Spectrometer, which utilizes a tungsten excitation source and produces X-rays of energy up to 40 keV. Fluorescent X-ray detection is done using a Si PiN diode capable of less than 280 eV FWHM at 5.95 keV Mn Kα line. The channel width, the grouping (bin) of collected X-rays, is 19.61 eV. While this arrangement leads to a polychromatic probe beam, which complicates analysis, it is considerably faster and more economical than monochromatic systems. The Innov-X software analyzes the collected spectra and calculates the elemental levels in parts per million (ppm) for the sample matrix. Since the films on our samples are different from the assumed evenly mixed matrix, the ppm data is considered arbitrary. Because of this, we treat it as an arbitrary unit used for correlation analysis and production control only. Film thicknesses were measured using a Tencor Instruments Alpha-Step profilometer. Statistical analysis of the data was performed using Minitab 15 statistical software. Thermal modeling of the new heater design was done using ANSYS Fluent 12.0.

XRF THICKNESS MEASUREMENTS
In order to pursue optimization of cell performance, it has become necessary to develop a metric for quantities of CdS and Cu present in the device. By combining this roughness and interdiffusion independent metric with interdiffusion data gathered with QE measurements it is possible to describe response surfaces for process optimization. Here we describe the development of a structure independent CdS thickness metric derived from XRF data.

If the incident X-ray beam is sufficiently collimated and narrow relative to sample thickness variations, the resulting X-ray signal is proportional to the mass of Cd per unit area and can be related to layer thickness. A representative spectrum is shown in Fig. 1. Characteristic Kα peaks for Cd, Te, Sn (from the SnO₂ TCO), and the Cu peak region are labeled.

The peaks in Fig. 1 are superimposed on a smooth background resulting from elastic and inelastic scattering of the incident beam. The peak size, \( C(E_i) \), can be determined by Eq. 1, where total count in the channel is \( S(E_i) \), centered on \( E_i \), and background count is \( B(E_i) \) at \( E_i \). The background signal is derived from a blank sample (glass/TCO only) reference spectrum \( R_{E_i} \) appropriately modified for attenuation due to the \( n \) overlying films as shown by Eq. 2, where \( \theta \) is

![Figure 1 XRF spectrum of CdS/CdTe films on glass/TCO with Cu back contact.](image1.png)

![Figure 2 Film thickness correlations to XRF measured levels in (a) CdTe and (b) CdS films on glass/TCO using 5 minute measurement duration.](image2.png)

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The Innov-X measurement system provides Cd, Te, Sn, and Cu levels at ppm levels within the measured matrix. Sulfur cannot be measured by this XRF system. From this data a correlation between measured elemental levels and thickness of layers was made. Fig. 2 shows this empirical correlation from samples of various CdS and CdTe thicknesses deposited independently on glass/TCO structures. Although the CdTe is deposited with a 1:1 atomic ratio, the difference in the Cd and Te measurement levels is due to the efficiency of excitation by the polychromatic beam and the calibration/calculation algorithm of the Innov-X XRF system. This correlation analysis, made with the factory calibration and calculation algorithms of the XRF equipment, is able to accurately predict CdTe thickness with the derived empirical model. The model for CdS thickness is poor and needs improvement. The variations in this model could be due to the variability of the profilometer thickness measurements, the XRF measurements, and the counting uncertainty in the calculations. These factors need to be explored. The XRF data was also collected over 5 minutes, which is poor for an in-line process control in our manufacturing system. A new calibration model for accurate and fast measurements is needed.
incident beam angle, \( \phi \) is center of the exit beam solid angle extending to the detector, \( \mu \) is the attenuation coefficient, and \( t \) is the layer thickness. The fractional uncertainty of counts, \( F \), for a single bin is given by Eq. 3 [5]. This indicates that a small signal on top of a large background leads to a large fractional uncertainty, implying a fundamental limitation imposed by a non-monochromatic X-ray probe beam. The fractional uncertainty in counts under an entire peak is given by Eq. 4. The number of counts in each bin is proportional to the time that the spectrum is collected, so that the fractional error is given by Eq. 5, where \( c(E_i) \) is the count rate in the channel centered on \( E_i \), and \( t \) is the spectral collection time. The fractional uncertainty in measurement determines the Lower Detection Limit (LDL) for trace elements as well as the accuracy of thickness measurements. From the count rate spectrum in Fig. 1, we can estimate the sensitivity of the measurement system to various elements at different measurement durations, such as 5 minutes used for Fig. 1 and the desired 30 seconds (Table 1). These results again indicate that the CdTe thickness measurements with XRF are acceptable, while the CdS measurements need improvement.

The low fundamental uncertainties in thickness for a 30 sec. measurement are a consequence of high count rate (160-800 count/sec) for Cd and Te K\( \alpha \) X-rays, indicating that a properly calibrated system with a robust background subtraction algorithm would have sufficient resolution for use in thin film thickness monitoring.

The probability that an incoming X-ray will generate a fluorescent X-ray which exits the film in a small solid angle centered about \( \phi \) can be calculated, assuming isotropic fluorescence, by Eq. 6, where \( K \) is the probability the fluorescence X-ray is measured by the detector. Since the X-ray probe energy is distributed in energy, we must integrate this to determine the probability of an incoming X-ray causing detectable fluorescence. This is given by Eq. 7. The incident spectrum in our hardware is the spectrum of the incident beam angle, \( \phi \). Energy flux is distributed in energy, we must integrate this to determine the probability of an incoming X-ray causing detectable fluorescence.

\[
\sum_i C(E_i) = \sum_i S(E_i) - B(E_i) \quad (1)
\]

\[
B(E_i) = \text{Ref}(E_i) \prod_{n} \exp(-\mu_n(E_i) t_n \sec(\theta) \sec(\phi)) \quad (2)
\]

\[
F_i = \frac{\text{Ref}(E_i)}{C(E_i)} = \sqrt{\frac{S(E_i)}{B(E_i)}} \quad (3)
\]

\[
F_{in \text{Peak}} = \frac{\sum_{i \in \text{Peak}} C(E_i)}{\sum_{i} C(E_i)} \quad (4)
\]

\[
F(t) = \frac{\sum_{i} C(E_i)}{\sum_{i} C(E_i)} t^{-1/2} \quad (5)
\]

\[
P(E_i) = K \int_{0}^{E_i} \exp(-\mu_{Al}(E_i) \sec(\theta) x) \cdot \mu_{Fi}(E_i) \cdot \exp(-\mu_{Al}(E_{Fl}) \sec(\phi) x) \sec(\theta) \: dx \quad (6)
\]

\[
P = \frac{\sum_i P(E_i) I_0(E_i)}{\sum_i I_0(E_i)} \quad (7)
\]

\[
I_0(E_i) \propto \frac{E_{max}}{E_i} \exp(-\mu_{Al} t_{Al}) \quad (8)
\]

**XRF Cu MEASUREMENTS**

XRF can be used to measure the amount of Cu deposited for back contact formation. Consequently, it is important to understand the capabilities and limitations of these measurements. This was achieved using gage repeatability and reproducibility (GR&R) studies. Typically GR&R determines if measurements are robust regardless of opera-
tors. Due to the simple XRF interface and from previous studies, analysis of operator variation will not be repeated here. Instead, effects of live-time (time of X-ray collection when the detector is not saturated) on Cu measurement by the system were evaluated to determine accuracy of the measurements.

The first investigation was performed on ten samples with varied Cu treatments using ~600 and ~1200 second live-times, representing 15 and 30 minute testing times respectively with three replicates of each measurement. Due to program parameters, exact live-time could not be set, thus only approximate live-times could be achieved. The GR&R analysis determined percentage of measurement variability stemming from part-to-part variation, reproducibility (i.e., variation due to live-time setting), and repeatability (i.e., inherent machine variation). Cu content of CdS/CdTe structures, measured in ppm (considered arbitrary), produced by the XRF system was the measurement used for the GR&R analysis.

GR&R results computed by Minitab 15 statistical software are in Table 2, which shows the percentage variation contribution of each type of variation source. For the ten samples, which had a Cu range of ±250 ppm, the main variation in measurements comes from part-to-part variation, while repeatability and reproducibility variations are both small. Thus, it is concluded that XRF is a viable tool to determine large (>250 ppm) differences in deposited Cu. This range, however, is too large for process control to achieve good solar cells. To narrow the range in the samples, outlier Cu measurements were omitted in a second analysis of 7 samples with a Cu range of ±50 ppm. Part-to-part variation again dominates the variation while a rise in machine caused variations is seen. This suggests that XRF is acceptable for this narrower range. Poor repeatability is seen when the range is narrowed further (4 samples at ±15 ppm Cu) indicating the XRF may be poor at this range. However, the latter analysis does not include enough samples to be statistically significant and should be repeated with more samples in the same range. For all ranges, results show that variations in live-time setting (reproducibility) do not have a large effect on measured Cu content. Cu measurement with XRF appears to be robust to be performed at the lower live-time setting of roughly 600 sec. (15 min. of XRF operation) and can differentiate Cu levels in the ±50 ppm range. This indicates that XRF has promise for process control of Cu during manufacturing. A study with a smaller Cu range was conducted next to determine XRF is effective in production control.

The second study was performed with samples with a narrower range of Cu content. These were taken from the same run of our continuous in-line process. These samples are a better indication of a production style process control. The 15 samples were split into two categories: 10 with typical amount of Cu (approx 50 ppm) and 5 with trace amounts of Cu (approx. 15 ppm). The samples with trace Cu replicate the depletion of the Cu deposition material during production. This does not happen often, but nonetheless the information is useful for continuous production control. The GR&R results in Table 3 indicate that the two pools are significantly different and the simple XRF system can effectively differentiate between the two categories, as expected. A separate GR&R analysis was done on only the 10 typical Cu samples to demonstrate the measurement repeatability for a narrow Cu range. The results indicate the Cu content range to be approximately ±5 ppm and that the measurements exhibit acceptable repeatability error. This range is sufficient for the process control of the Cu treatment. We have demonstrated earlier that the appropriate Cu range for stable and effective devices is broad and much larger than the ±5 ppm Cu range we studied [7]. This indicates that the simple XRF system is a reliable tool for Cu process control on the production line and can effectively detect changes of greater than 10% of nominal in the samples.

<table>
<thead>
<tr>
<th>Sample Size</th>
<th>10 Samples</th>
<th>7 Samples</th>
<th>4 Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu range (ppm, arb. units)</td>
<td>±250</td>
<td>±50</td>
<td>±15</td>
</tr>
<tr>
<td>Repeatability</td>
<td>0.03%</td>
<td>0.49%</td>
<td>13.18%</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>0%</td>
<td>0.02%</td>
<td>0%</td>
</tr>
<tr>
<td>Part-to-Part</td>
<td>99.97%</td>
<td>99.49%</td>
<td>86.82%</td>
</tr>
</tbody>
</table>

Table 2 Percent variation contribution by source in XRF Cu measurements analyzed using GR&R.

<table>
<thead>
<tr>
<th>Variation Source</th>
<th>15 Samples</th>
<th>10 Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu range (ppm, arb. units)</td>
<td>±20</td>
<td>±5</td>
</tr>
<tr>
<td>Repeatability</td>
<td>0.48%</td>
<td>10.66%</td>
</tr>
<tr>
<td>Part-to-Part</td>
<td>99.52%</td>
<td>89.34%</td>
</tr>
</tbody>
</table>

Table 3 Percent variability contribution by variation source in XRF Cu measurements analyzed using GR&R.

Further investigation into this technique should include: (a) correlating measured Cu with stability and performance characteristics to identify process control limits, (b) testing the reliability of Cu measurements with shorter collection times, and (c) improving Cu measurements by developing a better calibration model relating observed X-rays to Cu content in the films.

NEW R&D SYSTEM DESCRIPTION

We have updated our continuous in-line system to be more flexible for experimental research. The improvements include the use of a magnetic substrate transport system coupled with a load lock. This improvement allows us to easily change process condition, process sequences, and substrate materials, while tightly controlling process parameters. The addition of the load lock has reconfigured substrate motion through the system and
required a redesign of the sublimation crucibles. The new R&D system improves our experimental efficiency and requires a smaller number of glass substrates. More information on this system and results of experiments will be forthcoming in the future.

**NEW HEATER AND THERMAL MODELING**

Our CSS-based deposition process uses a graphite crucible as the sublimation source. The common heating method of this crucible uses high intensity IR bulbs. Due to the radial emission of energy from the IR bulbs, controlling the energy that is not directly incident on the crucible surface is not trivial and leads to inefficient power use and potential heating of the surrounding shielding and support structures. Utilizing a conductive heating method will improve the efficiency of the heating unit and reduce the complexity of the radiation shielding surrounding the crucible and the heating hardware.

To facilitate conductive heating of the crucible, a coiled NiCr wire heating element was designed to be embedded into the graphite crucible. This arrangement allows direct conduction into the crucible, improving energy use and permitting better temperature uniformity throughout the crucible. The heating coil is made from NiCr 80 resistive heating wire that has been designed to output 1,200 W at 120 VAC. A castable, electrically insulating, alumina-based ceramic is used to embed the NiCr coil in a machined serpentine groove at the bottom of the graphite crucible. The whole unit is then installed in stainless steel racking and topped with a graphite substrate heater using the same embedded heating element.

<table>
<thead>
<tr>
<th>Location</th>
<th>Computation Temp (°C)</th>
<th>EXP Temp (°C)</th>
<th>Temp Diff (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>at_coil</td>
<td>556.6</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>bot_mid</td>
<td>555.0</td>
<td>550.4</td>
<td>4.6</td>
</tr>
<tr>
<td>pocket</td>
<td>548.0</td>
<td>518.9</td>
<td>28.2</td>
</tr>
<tr>
<td>top_mid</td>
<td>415.0</td>
<td>406.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Table 4 CFD Computation Temperatures vs. Experimental Temperatures at various source locations.

Computational fluid dynamics (CFD) thermal modeling was used to evaluate the thermal gradients within the graphite crucible and to determine heating uniformity and maximum temperature. Due to the complexity of the coiled heating wire the heating was modeled by applying a flux of 72.5 kW/m² to the cylindrical surface of the outside diameter of the heating coil. This heat flux equates to 1200 W over the whole surface area of the modeled heating coil surface. An initial 2D model of only the main crucible without racking shielding or top source was created to predict thermal uniformity and steady state temperature. The initial results showed acceptable temperature uniformity in the horizontal plane of the design and predicted a steady state temperature in the sublimation pocket of 525 °C.

Subsequent testing of a prototype heating unit matched the steady state temperature within 5 °C.

A full 3D thermal model and a prototype of the sublimation unit were then created. To accurately model the unit at operating conditions, the top heater was set to a steady operating temperature of 400 °C, which is the typical operating temperature of the top heater. The main bottom heating unit was given the same heat flux to emulate a 1200 W heater. Point surfaces were created in the CFD model to monitor temperature at approximately the same locations as thermocouples in prototype test (Fig. 5).

The initial CFD run had steady state temperatures 19-20°C higher than the actual experimental data. This was caused by using the theoretical heat output of the heating coil. The actual voltage and resistance of the heater were significantly lower than expected. The actual heat output of the heating coil was found to be 1,121 W. The CFD model was then re-evaluated with the actual heat flux. Comparison of both indicates that the steady state temperatures matched the experimental data within 10°C (Table 4). The temperature discrepancy at the pocket location is due to poor placement of the thermocouple during prototype testing. The CFD model’s ability to match the steady state temperatures of experimental data verifies that it is useful in design analysis. Thus, CFD modeling can be used to investigate the internal temperature uniformity in the crucible. From the plot of contours of steady state temperature (Fig. 6), we can see that the core temperature around the sublimation pocket is a steady temperature of approximately 550°C and has good temperature uniformity in the horizontal plane.
The CFD model will be used in the future for designing additional shielding to help contain heat loss and elevate the final steady state temperature of the sublimation crucible. In addition, the CFD model will be used to test each sublimation station, at operating temperatures, to ensure correct substrate temperatures and conditions. Future modeling efforts will also work on modeling the material flow during the sublimation process and interactions with advanced heating control systems.

**CONCLUSIONS**

XRF has shown to be a useful technique to measure CdS and CdTe layer thicknesses using linear fit of empirical data with factory calibrated simple XRF equipment. Additional theoretical analysis shows that a better calibration model can be used to measure the thickness in as short as 30 seconds of CdTe. Measuring CdS thickness requires additional improvements to the calibration and calculation techniques or longer measurement durations. Statistical variation of XRF measured Cu levels in CdTe films showed promise of XRF use for accurate process control of Cu in large scale manufacturing. Future experimentation will be done on our updated deposition system to further validate the use of XRF for Cu measurements and correlate to performance characteristics. Updates to the experimental system include NiCr wire heating of deposition sources. Thermal modeling shows that the new heating design will reach desired operating temperature and maintain good temperature uniformity throughout the horizontal plane of the crucible. The new design is expected to utilize less energy than typical IR bulb heating schemes. Future work will focus on building models that simulate effects of sublimation and advanced heating control systems.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


