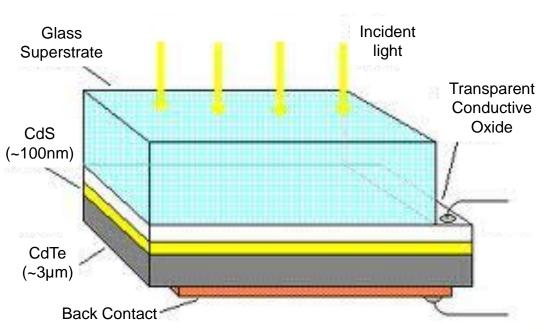




Measurement of CdTe Ratio for Composition Control

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CdTe Solar Cell



- CdTe is a very good choice for a thin film solar material.
- CdTe has a nearly ideal bandgap for the solar spectrum. Potential efficiency is very high at 29%.
- CdTe has a high absorption coefficient for light allowing for thinner films.
- CdTe can be deposited very quickly achieving 50:50 stoichiometry. Being able to do this step fast and at low cost is one of the reasons for First Solar's success.



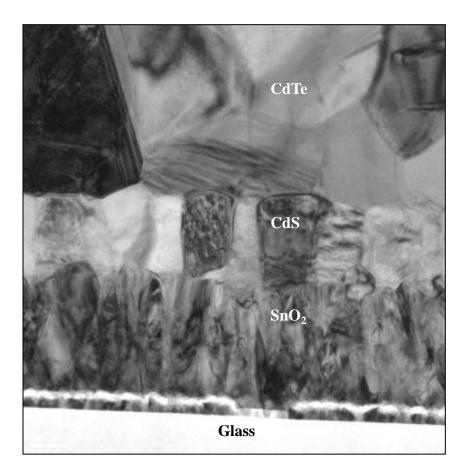
- Lately there have been many news stories about the supremacy of silicon solar cells and various thin film aspirants falling by the wayside.
- Cost of silicon is often given as the reason at less than \$20/kg.
- Silicon is not winning because of material cost.
- Silicon is succeeding because of manufacturing costs.
- First Solar has low materials costs, low deposition costs, low framing cost, low manufacturing costs.



- CdTe grains should be as large as possible, extending completely through the film to minimize grain boundaries.
- 50:50 CdTe has limited conductivity. Cu is added as a p-type dopant which improves conductivity.
- 50:50 CdTe as-grown is relatively small grained and has many defects/charge trap sites. A CI treatment leads to larger grains and seems to passivate many charge trap sites.

CdTe Layer Structure

EAG TEM Analysis of CdTe



- While Cu improves conductivity, add too much and it degrades the CdS heterojunction and decreases shunt resistance.
- Some researchers are looking at other ways to enhance CdTe conductivity.
- If CdTe can be made 'off-ratio', it can be made p-type or n-type.
- Recent work has shown that defects can be reduced, conductivity enhanced, and the need for doping and chloride treatment eliminated.
- However it is difficult to consistently achieve a non-stoichiometric ratio.



- Recent work by Razykov et al [1] has shown the desirable large grain structure can still be grown and resistance can be kept low for Cd:Te ratios of 0.86 and 1.1.
- The chloride treatment necessary for 50:50 is not needed.
- These are the driving forces to create and control non-stoichiometric ratio CdTe.
- T.M. Razykov, N. Amin, M.A. Alghoul, B. Ergashev, C.S. Ferekides, Y. Goswani, M.K. Hakkulov, K.M. Kouchkarov, K. Sopian, M.Y. Sulaiman and H.S. Ullal, "Effect of the composition on physical properties of CdTe absorber layer fabricated by chemical molecular beam deposition for use in thin film solar cells", J. Appl. Phys. **112**, 023517 (2012).

CdTe Phase Diagram =AG

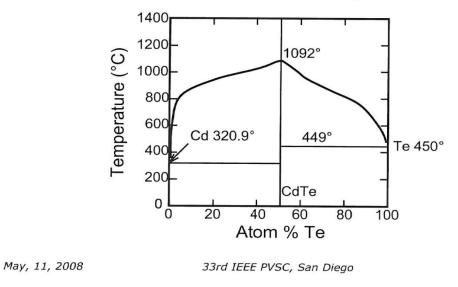
CdTe Phase Diagram

Evans Analytical Group

Only CdTe and endpoint Cd and Te phases

 \Box Very narrow single phase existence ~10⁻⁶ at.%

CdTe melts congruently with high liquidis temperature due to strong ionic Cd-Te bonding



- The phase diagram shows CdTe, Cd and Te are the only single phase materials.
- Therefore 'off-ratio' • will be a multi-phase material.

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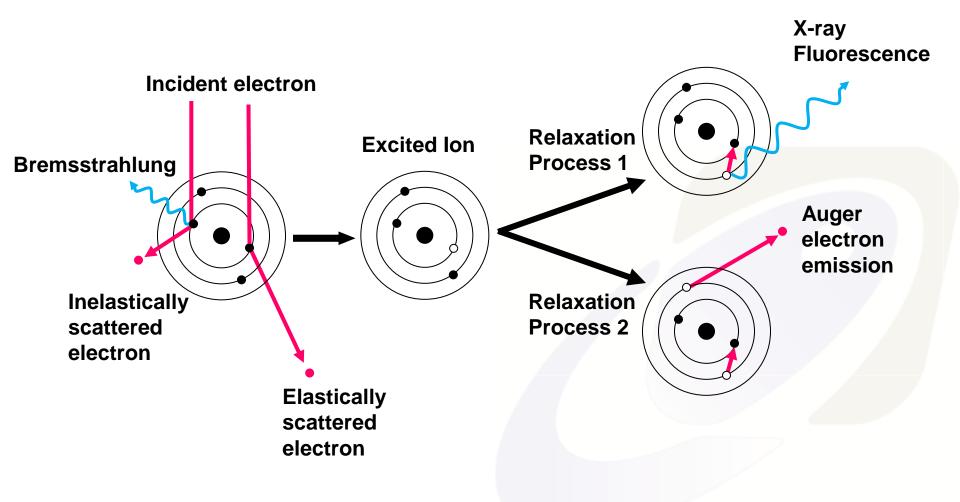
- For the analytical laboratory, our challenge is to accurately and reproducibly measure Cd:Te ratio.
- That means we need analysis techniques with good accuracy, and good precision.
- Accuracy can often be achieved by using a good standard. We use a Bridgeman grown single crystal CdTe reference.
- Very high precision can be achieved with LEXES for composition.
- Ratio changes with depth can be observed by SIMS.



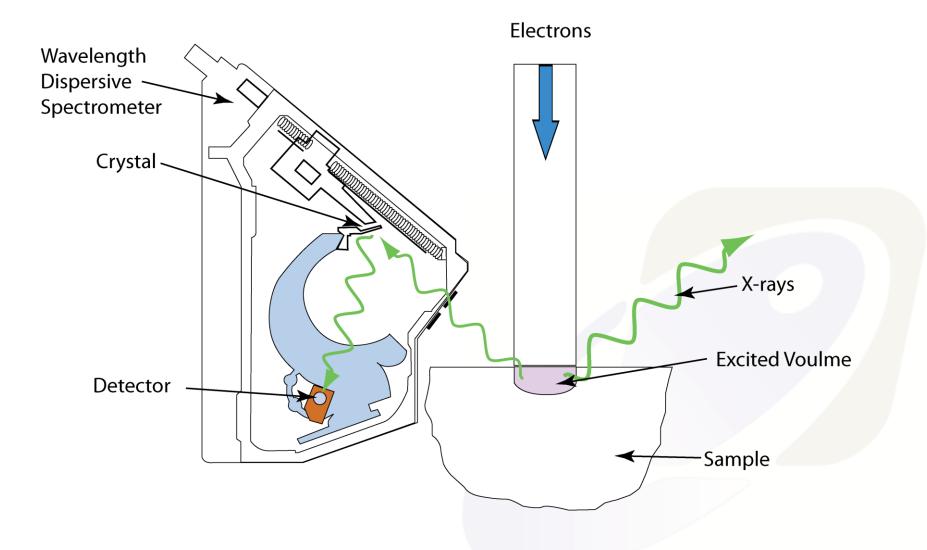
Low Energy X-ray Emission Spectrometry

LEXES





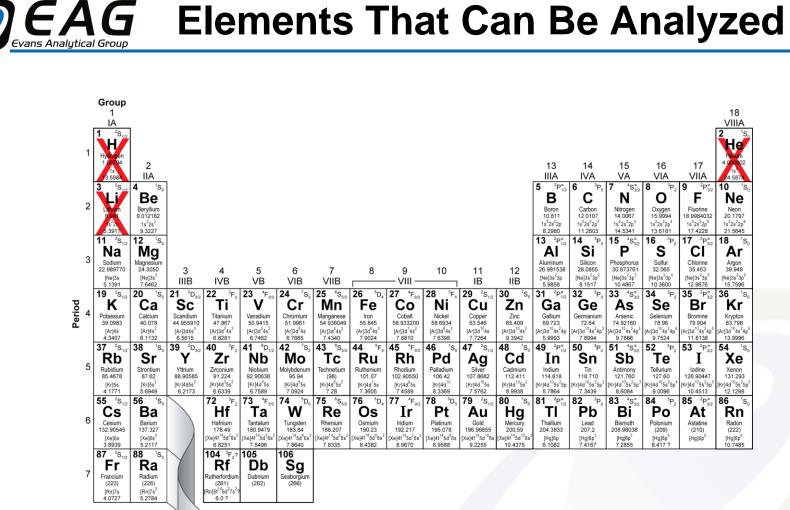




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DECAG LEXES: Theory/Background

- Sample is probed using a beam of mono-energetic electrons
 - Electron energies ranging from 0.2keV to 10keV can be used
 - Adjusting electron energy affects sampling depth
 - Depths from 1nm to 500nm can be probed
 - Spots as small as 30µm can be analyzed
- Characteristic X-rays are produced
 - Same X-rays as measured during EDS
- X-rays are detected/separated using Wavelength Dispersive Spectrometers (WDS)
 - Higher resolution of WDS resolves interferences
 - Higher sensitivity allows the measurement of dopants and very thin films (<2nm)



| S | 57 ² D _{3/2} | 58 ¹ G ₄ ° | 59 ⁴ I _{9/2} | 60 ⁵ I ₄ | 61 ⁶ H ^o _{5/2} | 62 ⁷ F ₀ | 63 ⁸ S [°] _{7/2} | 64 ⁹ D ₂ ° | 65 °H° | 66 ⁵ I ₈ | 67 ⁴ I ^o _{15/2} | 68 ³ H ₆ | 69 ² F ^o _{7/2} | 70 ¹ S ₀ | 71 ² D _{3/2} |
|------|----------------------------------|-------------------------------------|---------------------------------------|---------------------------------------|---|-------------------------------------|---|---------------------------------------|--|--------------------------------------|--|--------------------------------------|--|--------------------------------------|--|
| nide | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Но | Er | Tm | Yb | Lu |
| tha | Lanthanum | Cerium | Praseodymium | | Promethium | Samarium | Europium | Gadolinium | Terbium | Dysprosium | Holmium | Erbium | Thulium | Ytterbium | Lutetium |
| | 138.9055 | 140.116 | 140.90765 | 144.24 | (145) | 150.36 | 151.964 | 157.25 | 158.92534 | 162.500 | 164.93032 | 167.259 | 168.93421 | 173.04 | 174.967 |
| Ľ | [Xe]5d6s ² | [Xe]4f5d6s ² | [Xe]4f ³ 6s ² | [Xe]4f ⁴ 6s ² | [Xe]4f ⁵ 6s ² | [Xe]4f ⁶ 6s ² | [Xe]4f ⁷ 6s ² | [Xe]4f ⁷ 5d6s ² | [Xe]4f ⁹ 6s ² | [Xe]4f ¹⁰ 6s ² | [Xe]4f ¹¹ 6s ² | [Xe]4f ¹² 6s ² | [Xe]4f ¹³ 6s ² | [Xe]4f ¹⁴ 6s ² | [Xe]4f ¹⁴ 5d6s ² |
| | 5.5769 | 5.5387 | 5.473 | 5.5250 | 5.582 | 5.6437 | 5.6704 | 6.1498 | 5.8638 | 5.9389 | 6.0215 | 6.1077 | 6.1843 | 6.2542 | 5.4259 |
| | 89 ² D _{3/2} | 90 ³ F ₂ | 91 ⁴K _{11/2} | 92 ⁵L ₆ ° | 93 ⁶ L _{11/2} | 94 ⁷ F _o | 95 ⁸ S ^o _{7/2} | 96 °D ₂ ° | 97 ⁶ H [°] _{15/2} | 98 ⁵ I _a | 99 ⁴ I ^o _{15/2} | 100 ³ H ₆ | 101 ² F ^o _{7/2} | 102 ¹ S ₀ | 103 ² P° _{1/2} ? |
| ides | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Em | Md | No | |
| ţ | Actinium | Thorium | Protactinium | Uranium | Neptunium | Plutonium | Americium | Curium | Berkelium | Californium | Einsteinium | Fermium | Mendelewium | Nobelium | Lawrencium |
| AC A | (227) | 232.0381 | 231.03588 | 238.02891 | (237) | (244) | (243) | (247) | (247) | (251) | (252) | (257) | (258) | (259) | (262) |
| / | [Rn]6d7s ² | [Rn]6d ² 7s ² | [Rn]5f ² 6d7s ² | [Rn]5f ³ 6d7s ² | [Rn]5f ⁴ 6d7s ² | [Rn]5f ⁶ 7s ² | [Rn]5f ⁷ 7s ² | [Rn]5f ⁷ 6d7s ² | [Rn]5f ³ 7s ² | [Rn]5f ¹⁰ 7s ² | [Rn]5f ¹ 7s ² | [Rn]5f ¹² 7s ² | [Rn]5f ¹³ 7s ² | [Rn]5f ¹⁴ 7s ² | [Rg]5f ¹⁴ 7s ² Xp? |
| | 5.17 | 6.3067 | 5.89 | 6.1941 | 6.2657 | 6.0260 | 5.9738 | 5.9914 | 6 1979 | 6 2817 | 6 42 | 6 50 | 6 58 | 6.65 | 4.9 ? |

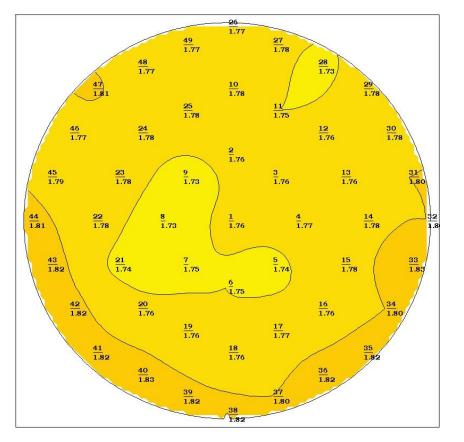


To convert the X-ray intensity (Peak-Background) into absolute concentration or dose, we must correct for the following:

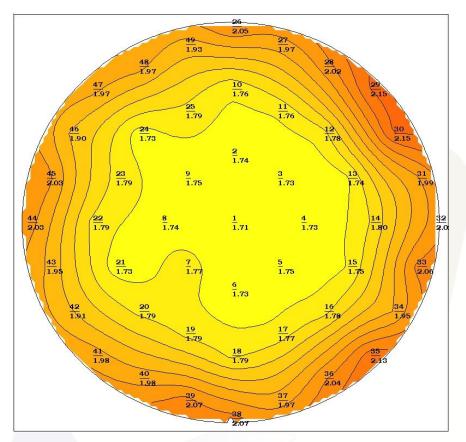
- Energy loss by the electrons as they penetrate the matrix,
- Efficiency of X-ray production at each depth, i.e. electron energy, and
- Probability of the X-ray escaping the matrix from the depth of its production.

EXAMPLE 50Å Al_2O_3 Deposited by ALD

Standard Cycle



Avg. Al Dose = 1.78E16 atoms/cm² %RSD = 1.53%



Short Cycle

Avg. Al Dose = 1.88E16 atoms/cm² %RSD = 7.31%



Model for electron interaction and X-ray emission from CdTe has been developed. As a result we can:

- Determines that Cd:Te ratio to within 0.1 at%
- Calibrated vs. CdTe single crystal.
- Determines differences in Cd:Te ratio to within 0.01 at%.



| Location | Cd/Te Ratio | | | | | |
|-----------|-------------|--|--|--|--|--|
| 1 | 0.950 | | | | | |
| 2 | 0.962 | | | | | |
| 3 | 0.968 | | | | | |
| 4 | 0.956 | | | | | |
| Average | 0.958 | | | | | |
| Std. Dev. | 0.008 | | | | | |

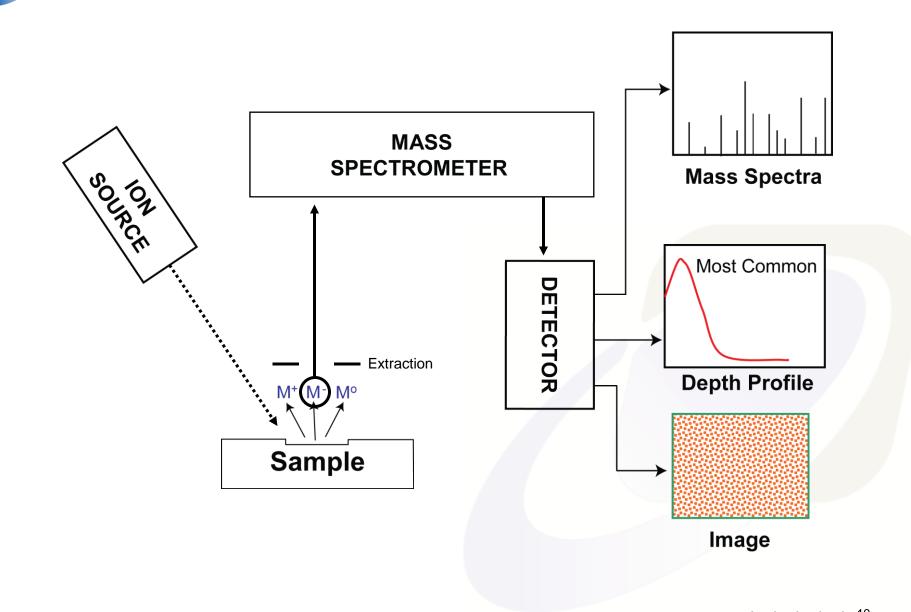
- Here we see 4 LEXES measurements from 4 locations on a sample.
- The maximum difference in the ratio between locations is 0.018 or 1.9%.



Secondary Ion Mass Spectrometry

SIMS

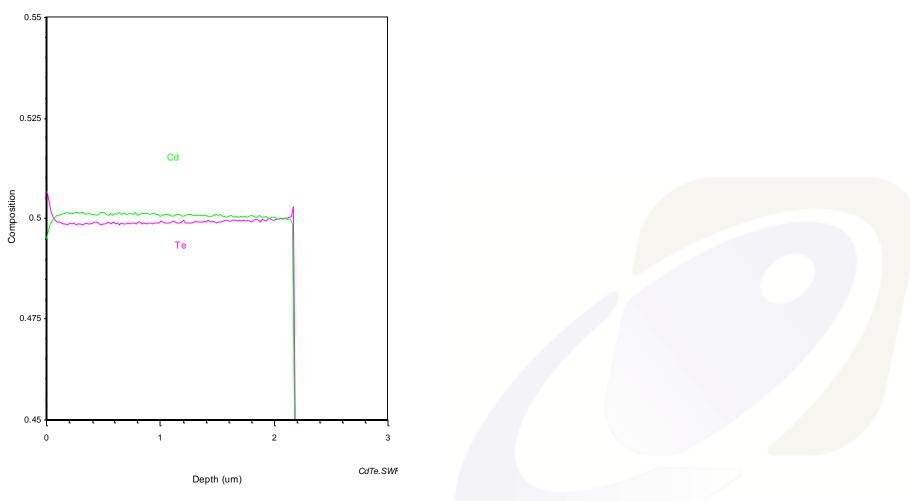






- SIMS is well know for trace element profiling with high sensitivity.
- Why use SIMS for matrix level profiling?
- Short answer: Speed
- With a proper standard, SIMS accuracy is good and depth resolution is excellent.
- Precision during the profile is similar to LEXES.

CdTe Ratio Analysis by SIMS



SIMS profiles provide Cd and Te composition variation at different depths.



- CdTe ratio control is an interesting concept that appears to hold promise for increased efficiency at lower cost.
- The challenge for an analytical laboratory is to measure small differences in composition with high accuracy and precision.
- Composition needs to be measured both laterally and through-thickness.
- LEXES and SIMS provide effective measurements meeting analytical requirements for accuracy and precision.