INVESTIGATION OF Cu-In-Ga-Se THIN FILM GROWTH DYNAMICS FOR HIGH EFFICIENCY SOLAR CELLS

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Applied Physics)

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Date February 24, 2003

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ABSTRACT

$Cu(In,Ga)Se_2$ (CIGS)-based solar cells are promising for photovoltaic applications. The growth dynamics of CIGS thin films were investigated based on the three stage Physical Vapor Deposition (PVD) growth process to deposit the films. Using this process, the highest efficiency achieved so far for a CIGS-based solar cell is 19.2 %. The objective of this investigation is to develop the fundamental understanding of the growth process and how it leads to film properties that are responsible for such a high efficiency, and also identify those properties that need to be enhanced further toward achieving efficiencies greater than 20 %.

The experimental approach is to interrupt the film growth process at critical points along the growth pathway and examine the material properties as the film develops toward its final stage. These critical points were chosen to correlate with certain phases on the CIGS pseudo-binary tie-line. Several CIGS thin films with Cu/(In+Ga) ratio ranging from 0 to 30 % and two Ga/(In+Ga) ratios (~30 % and ~60 %) were prepared. It is found that in the three-stage process, the growth kinetics, substrate temperature profile, and reaction time will make the outcome of local equilibria unique to the growth process. Key results are: (1) stoichiometric $(In,Ga)_2Se_3$ was prepared. By adding Cu, the lattice is mainly altered through the c-axis, the chalcopyrite structure starts to appear, and homogeneity in the Cu distribution in our CIGS films improves. CIGS films with 6-11% Cu shows the strongest lamellar structure which is indicative of the presence of the defect-chalcopyrite phase. Films with higher Ga content have smaller grains. (2) At the Cu-rich stage of the three-stage process, the film contains the α-CIGS phase (as the primary phase) and $Cu_{2-x}Se$ as a secondary phase. The grains of the two phases are coherent and appear as a large single grain by Scanning Electron Microscopy (SEM). As the film transitions to In(Ga)-rich, the large grains appear to decompose into smaller grains. In the Cu-rich sample, two structurally different $Cu_{2-x}Se$ phases with different x-values exist with the CIGS major phase. A cubic phase exists on the CIGS crystallites, and a tetragonal phase exists between the CIGS grains. It is believed that the tetragonal $Cu_{2-x}Se$ is the first to form during the 2nd stage of the three stage growth process, and serves as the host lattice for In and Ga from the $(In,Ga)_2Se_3$ in stage one, resulting in the formation of the CIGS tetragonal lattice. The cubic phase of $Cu_{2-x}Se$ forms at the point when Cu exceeds stoichiometry, and nucleates on the already formed CIGS crystallites. At the transition point from Cu-rich to In(Ga)-rich, conformal and coherent sub-domain boundaries which cannot be seen by SEM are formed. These sub-boundaries are the precursors for grain-boundaries, which materialize when the film becomes In(Ga)-rich, and they also serve as a stress (and thus defects) relief mechanism; (3) Evolution of the intrinsic native defects depends on the dynamics of the reaction pathway, i.e., the compositional changes that occur when the film transitions from Cu-rich to In(Ga)-rich. For CIGS-based devices with Ga/(In+Ga) of 30%, acceptor-like traps dominate in samples where CIGS grains do not go through the Cu-rich to In(Ga)-rich transition, whereas donor-like traps dominate in In(Ga)-rich samples. Therefore, a clear transformation of defects from acceptor-like to donor-like traps can be seen. The activation energies of these traps range from 0.12 to 0.63 eV. Also, it is observed that NaCN treatment eliminates a deep minority trap in the In(Ga)-rich devices. For CIGS-based devices with Ga/(In+Ga) of 60%, only majority-carrier traps were detected. These traps again range from shallow to deep. The carrier concentration is the highest for Cu-rich CIGS and decreases as the material becomes more In(Ga)-rich. All our Deep Level Transient Spectroscopy (DLTS) data for low- and high-Ga devices show that the charge-carrier emission rate obeys the Meyer-Neldel rule; and (4) the highest concentration of defect states in three-stage grown CIGS material is generated at the end of the 2nd stage. Reducing these concentrations is beneficial to device performance. It was shown that modifying the growth process by introducing an annealing step after the 2nd or 3rd stages reduces the concentration of defects significantly and enhances device performance.

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