PhD thesis

Cr-doped ZnS for Intermediate Band Solar Cells

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Abstract

Intermediate band solar cells (IBSCs) can potentially be highly efficient solar cells. This thesis presents the growth and characterization of highly doped chromium doped zinc sulfide (Cr:ZnS) films for use in IBSCs. The films were grown by pulsed laser deposition (PLD) and molecular beam evaporation (MBE). In addition, prototype devices were made to test the materials.

The films were deposited onto p-type Si(100) and quartz substrates. In PLD films, a single target consisting of Cr particles ($20 - 100$ μm) embedded in a Cr:ZnS matrix was used and the Cr content in Cr:ZnS films was adjusted in the $2.0 - 5.0$ at.%, by varying the laser fluence or the number of pre-ablation pulses. In MBE films which are made by co-deposition of ZnS and metallic Cr, the Cr content varied in the range $0 - 7.5$ at.%.

The crystallinity of films was seen to depend strongly on the method of growth. Introducing Cr into ZnS reduced the grain size in both methods, but the average grain size was typically larger in MBE grown films. PLD resulted in smoother films with a single preferred crystal orientation. X-ray diffraction (XRD) results on all the PLD films showed preferred crystalline orientation along the [111] direction in zincblende or along [001] direction in wurtzite, but the MBE films had two additional peaks in their XRD patterns. Zincblende and wurtzite phases could not be distinguished by XRD alone. Further studies by transmission electron microscopy revealed that the main phase in PLD films with ~ 4 % Cr was wurtzite. High densities of stacking faults were also observed in Cr:ZnS films.

Spatial variation in the local chromium content in PLD films was found, with local Cr increases associated with reduced Zn content. X-ray photoelectron spectroscopy showed that Cr^{2+} is the major Cr valence state in both PLD and MBE films, while Cr^0 and possibly Cr^{3+} valence states were also present. These results indicate that the majority of Cr atoms substitute for Zn in Cr:ZnS, but that Cr may also reside in interstitial sites.

For optical properties, spectroscopic ellipsometry was performed. Introducing Cr into ZnS resulted in Cr-related sub-bandgap absorption. The sub-bandgap absorption increased with increasing Cr content, and a higher growth temperature, but did not depend on the method of growth, within the limits of temperature attainable in both techniques. From these studies, it is concluded that PLD can be used to deposit highly textured films with strong sub-bandgap absorption. Based on material characterization studies, PLD is found to be more promising than MBE for the growth of Cr:ZnS films suitable for IBSCs.

Two types of solar cell devices were fabricated. The first was single hetero-junction (SHJ) cells consisting of a single Cr:ZnS (or ZnS) film on the p-type Si substrate. The as-deposited ZnS and Cr:ZnS films made by PLD were (weakly) n-type. The second device had an additional n-doped Al:ZnO film on top of the Cr:ZnS films, resulting in a double hetero-junction (DHJ) cell. The effect of Cr:ZnS layer thickness was investigated, and the performances were simulated. The short circuit current density for the best DHJ cells was higher by a factor of about 27 for the device with Cr:ZnS, compared to the device with undoped ZnS. This is caused by higher absorption of sub-bandgap photons and improved transport properties. Potential negative effects of Shockley-Read-Hall recombination associated with Cr-related defects were less important than the improved absorption and transport properties due to the Cr inclusion.