Solar photovoltaics is considered as one of the most promising techniques for supplying clean, sustainable and renewable energy. II-VI and III-V semiconductor materials have attracted much interests for developing economically viable photovoltaic (PV) thin-film solar cells. Using the approach of multilayer structures, thin-film PV tandem cells should be able to overcome the Shockley-Queisser limit and achieve high-efficiencies in excess of 50%. Material and device characterization becomes an important task not only for quality control in the expanding PV industry but it also remains at the very heart of research and development of future PV materials.

The research described in this dissertation involved the use of transmission electron microscopy (TEM) to characterize the structural properties of II-VI and III-V compound semiconductor quantum dots (QDs) and dilute-nitride GaAsN thin films grown by molecular beam epitaxy (MBE) for PV applications. The samples investigated included CdTe QDs grown on ZnTe/GaSb hybrid substrates, InAs QDs incorporated with GaAsSb barrier layers grown on GaAs substrates, InAs QDs incorporated with AlAs/GaAs spacer layers grown on GaAs substrates, and dilute-nitride GaAsN thin films grown on GaAs substrates. Throughout the work, a comprehensive description of structural properties and correlation with the optoelectronic properties and device performance will be presented. Some insights for future development of the PV solar cells will be provided.