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Optical Properties of Zinc Ferrite Nanoparticles Embedded in Zinc Oxide Thin Films Investigated by STEM, EELS and CL

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To reduce shading losses in photovoltaic (PV) cells, a transparent conducting oxide (TCO) top layer can be introduced to replace the traditional silver contacts. The TCO should have a band gap exceeding 3 eV in order to be transparent to visible light. Meanwhile, the 1.1 eV band gap of silicon leads to significant losses in efficiency as much of the energy absorbed is lost as heat. In this contribution we explore introducing optically absorbing particles into the TCO in the form of zinc ferrite nanoparticles with a band gap of 2 eV [1], [2]. Such a TCO layer could then be incorporated into a larger multi-junction PV cell. We first investigate the formation and optical properties of zinc ferrite in bulk zinc oxide (ZnO), and then explore the formation of such particles in ZnO thin films grown by pulsed laser deposition (PLD).

Bulk samples were prepared by mixing powders of ZnO and iron oxide (Fe_2O_3) and subsequent heat treatment. X-ray diffraction and Transmission Electron Microscopy (TEM) confirmed the presence of nanoparticles of the zinc ferrite ($ZnFe_2O_4$) embedded in ZnO, thereby forming a composite. Cathodoluminescence (CL) measurements on these bulk samples showed increased luminescence at 2 eV compared to a ZnO reference, suggesting that the $ZnFe_2O_4$ nanoparticles are optically active at the relevant wavelengths (Fig. 1). Hence, the material system is promising as an absorbing TCO top cell layer in PVs. As bulk materials have poor applicability to PV devices, we investigated the formation of the nanoparticles in thin films.

Thin films were grown with multilayers of ZnO and Fe_2O_3 deposited on a silicon (Si) substrate using PLD, with a ratio of 4.3 at.% Fe to Zn. TEM specimens were prepared for cross-sectional observations by mechanical grinding and finished with Ar-ion milling in a Gatan Precision Ion Polishing System PIPS II. Scanning transmission electron microscopy (STEM), energy-dispersive x-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) were conducted in a Cs-corrected, monochromated Thermo Fisher Scientific Titan G2 60–300 kV microscope, equipped with a Gatan GIF Quantum 965 spectrometer, and Super-X EDS detectors. STEM imaging and EDS chemical analysis were performed at 300 kV, and band gap measurement was done at 60 kV to minimize the effect of Cherenkov radiation [3].

After annealing the film at 750 ℃ for 1 hour in air, we observed the presence of $ZnFe_2O_4$ nanoparticles embedded in the ZnO thin film (Fig. 2). Structural and chemical characterization was performed with HR-imaging, diffraction, and STEM-EDS, confirming that the nanoparticles are $ZnFe_2O_4$ spinel structures. The nanoparticles are predominantly located in the vicinity of grain boundaries of columnar ZnO grains and have a large size variation ranging from about 5 nm to 100 nm. The ZnO grains were observed with a preferential growth of (001) planes parallel to the substrate, and the nanoparticles were found with an orientation relationship with respect to ZnO, described by [101] (-111) $ZnFe_2O_4$ || ZnO [100] (001).

STEM-EELS was performed on a $ZnFe_2O_4$ particle for band gap extraction. After removing the zero-loss peak, the onset of energy loss was found through a fitting procedure to be between 2.11 and 2.25 eV

depending on whether a linear or square root function was used for the fitting [4] (Fig. 3), in agreement with reported values of the $ZnFe_2O_4$ band gap [1, 2, 5].

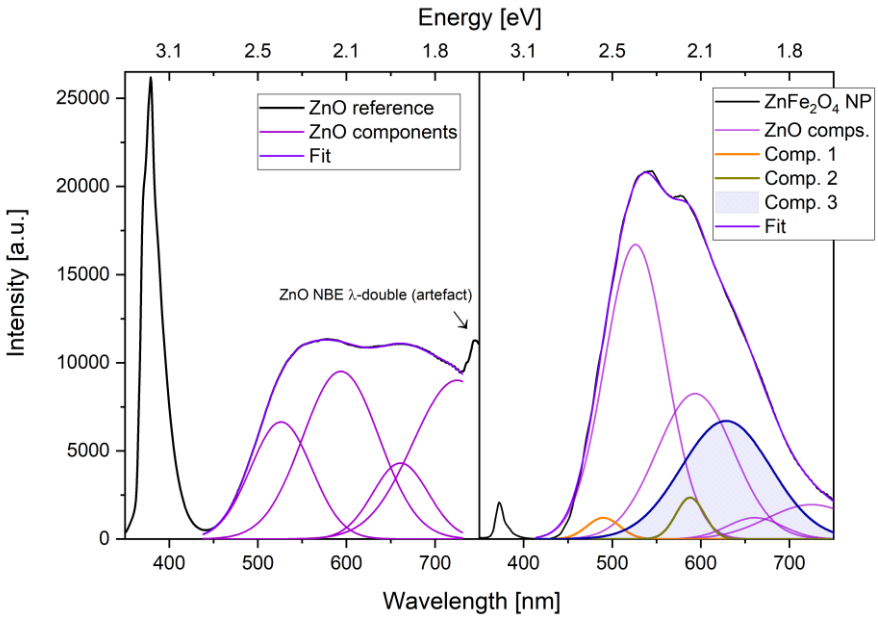

Figure 1. CL spectra from ZnO reference (left) and from a $ZnFe_2O_4$ particle (right) in the nanocomposite sample. Measurements on $ZnFe_2O_4$ shows increased luminescence around 2 eV compared to the ZnO reference. The fitting component 3 is not present in ZnO reference spectrum and decreased when measured far away from nanoparticle, i.e., in the ZnO matrix.

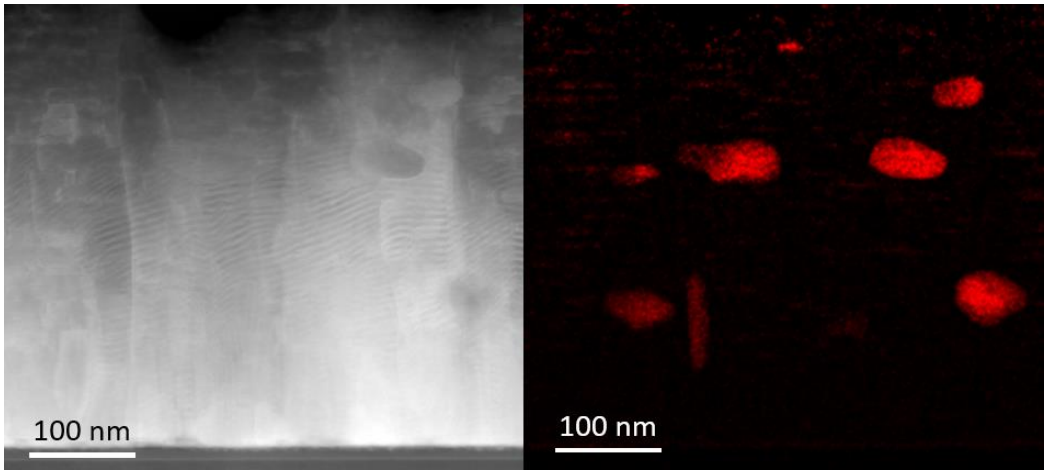

Figure 2. STEM-ADF image of ZnO thin film (left) with corresponding STEM-EDS map (right) revealing $ZnFe_2O_4$ particles in red, where signal intensity is from Fe-Kα1.

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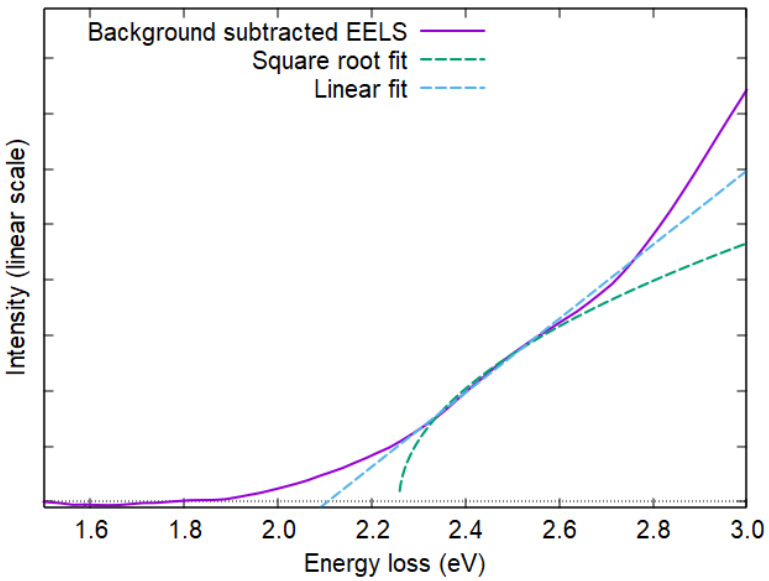

Figure 3. Background subtracted EEL spectrum from $ZnFe_2O_4$ nanoparticle in the ZnO thin film, fitted with a linear fit, and a square root fit as described by Rafferty and Brown [4]. Extrapolated to the energy loss axis, estimations of the band gap are extracted as 2.11 eV and 2.25 eV, respectively.

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