Formation of Nanoscale Composites of Compound Semiconductors Driven by Charge Transfer

New materials discovery often relies on mixing of different materials to create alloys or composites with properties tailored for specific applications. Composites, in particular, are an interesting class of materials because they can exhibit new functionalities and/or improved properties that the constituents do not possess [1-3]. Specifically, composites of semiconductors are widely used to create new materials with modified optoelectronic properties, band gaps and band offsets [4-8]. These materials are often formed by controlled deposition of, for example, multilayers or physical mixing (e.g. quantum wires and dots embedded in a host matrix. Composite formation during physical mixing relies on structural dissimilarities of the constituent materials, and can be driven by strain, lattice mismatch, spinodal decomposition or entropy.

The synthesis of a new type of semiconductor nanocomposite material is reported here. This is believed to be the first example of electronically driven phase separation in mixed materials and may provide a new way to engineer functional materials. This nanocomposite shows an unusual composition dependence of the electrical and optical properties. Two compound semiconductors with diametrically different electronic properties have been specially combined, intrinsically highly n-type conducting CdO and intrinsically highly p-type conducting SnTe to form the (SnTe)$_x$(CdO)$_{1-x}$ composite. In terms of electrical properties, the whole composition range of the composite can be divided into three well-defined regions: n-type for $0 < x < 0.34$, semi-insulating for $0.34 < x < 0.68$ and p-type for $0.68 < x < 1$. This behavior leads to a closer exploration of the structural properties of this composite material.

Figure. *(left)* TEM image of the (SnTe)$_x$(CdO)$_{1-x}$ composite ($x = 0.45$) reveals the presence of small crystallites with a 2–3 nm size. *(right)* Electrical properties of (SnTe)$_x$(CdO)$_{1-x}$ nanocomposites. Electrical conductivity, carrier concentration, and carrier mobility as functions of SnTe content for (SnTe)$_x$(CdO)$_{1-x}$ grown on glass substrates, determined by Hall-effect measurements at room temperature. The electrical properties vary from high n-type conducting in CdO-rich to high p-type conducting in SnTe-rich materials. A semi-insulating behavior is observed for films in the intermediate composition range.
Through careful TEM/SAD and XRD analysis the patterns can be matched to CdO for \( x < 0.13 \) and SnTe for \( x > 0.73 \). Showing the material is comprised of mainly a crystalline majority phase with of amorphous or nanocrystalline inclusions of the minority phase. In the insulating region XRD analysis suggested an amorphous or nanocrystalline composite due to the lack of diffraction in the composition range. However, careful TEM analysis identified small 2-3 nm crystallites for samples in this region. Comprehensive characterizations of the component materials have shown large charge transfer at the interface between SnTe and CdO [9]. This charge transfer stabilizes the formation of a fine, homogeneous composite of these two materials with the scale determined by the width of the interface charge accumulation layer [9]. Overall the materials properties can be explained by energy band structure derived byinterpolation of the electronic band structures of the end point compounds, CdO and SnTe.

The composition dependent optical properties of the nanocomposite are determined by two direct band gaps, at the gamma and L point of the Brillouin zone. This leads to a unique material with two equal direct band gaps and with type I band offsets for the nanocomposite with \( x=0.42 \). Illumination of this material results in separation of photoexcited charges in the k-space with electrons accumulating in the gamma point conduction band minimum and holes accumulating in L point valence band maximum.

The evolution of electrical properties of the composite from highly n-type conducting on the CdO-rich side to highly p-type conducting on the SnTe-rich side with the semi-insulating material in the intermediate composition range offers an interesting potential of creating tunnel junctions using a single material system. It should be noted that although this research was limited to \((\text{SnTe})_x(\text{CdO})_{1-x}\), the concept of the charge transfer driven formation of semiconductor composites is general and can apply to composite materials formed by semiconductors with distinctly different electronic properties.

References


**Primary Citation**


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