Structural Properties of (Sn,Mn)Se₂ - a New 2D Magnetic Semiconductor with Potential for Spintronic Applications

V. Kanzuyba¹, S. Dong¹, X. Li¹, T. Yoo¹,², X. Liu¹, S. Rouvimov³,⁴, S. Vishwanath³,⁵, D. Jena³,⁵,⁶, H. G. Xing³,⁵,⁶, M. Dobrowolska¹, and J. K. Furdyna¹

¹. Dept. of Physics, University of Notre Dame, Notre Dame, IN 46556, USA
². Dept. of Physics, Korea University, Seoul 136-701, Korea
³. Dept. of Electrical Engineering, University of Notre Dame, Notre Dame, IN 46556, USA
4. Notre Dame Integ. Imaging Facility, Univ. of Notre Dame, Notre Dame, IN 46556, USA
5. School of Electrical and Computer Engineering, Cornell Univ., Ithaca, NY 14853, USA
6. Dept. of Materials Science and Engineering, Cornell Univ., Ithaca, NY 14853, USA

Materials crystallizing in two-dimensional (2D) layer form have emerged as an important new materials family due to their unique electronic and optical properties that lay the ground for both basic and applied research. The new 2D semiconductor SnSe₂ crystallizing in hexagonal CdI₂ structure [1] (two-dimensional chalcogen-metal-chalcogen layers bonded by Van der Waals forces) is an important example of this class of materials, and is already recognized for its attractive optoelectronic properties [2]. Additionally, its 2D character holds promise for forming new materials combinations based on intercalation.

Our interest in SnSe₂ is motivated by using it as a basis for obtaining 2D systems with magnetic properties, which can then be exploited for new spintronic 2D functionalities [3]. We note here that our attempts to introduce magnetic ions by epitaxial growth into other 2D systems, such as the widely-studied transition metal dichalcogenides (e.g., MoSe₂) [4] and topological insulators (e.g., Bi₂Se₃) [5] have allowed only minute concentrations of magnetic ions (e.g., Mn) to be introduced into their respective lattices. In sharp contrast, however, in the case of SnSe₂ we were able to form 2D ternary Sn₁₋ₓMnₓSe₂ alloy films with values of x up to at least 0.65, with good crystalline quality. Our preliminary work on magnetic properties of these films (to be published elsewhere) has shown that they exhibit interesting magnetic behavior, with weak ferromagnetism persisting to above room temperature, thus making them of interest for spintronic applications. We note that these new properties arise directly from the unique capability of the SnSe₂ lattice to “accept” large concentrations of Mn while maintaining excellent crystalline quality.

In this paper we will focus specifically on the growth details of these new 2D magnetic alloys, and on the structural properties which they exhibit as a function of Mn content. The Sn₁₋ₓMnₓSe₂ films were grown by molecular beam epitaxy (MBE) on GaAs (111)B substrates, chosen because of the compatibility of this orientation with the hexagonal structure of the binary system SnSe₂. The epi-ready GaAs substrates were deoxidized at 580°C in the MBE chamber, annealed at ~ 600°C in Se flux, and cooled to 150°C prior to growth of Sn₁₋ₓMnₓSe₂. While cooling, the GaAs substrate was exposed to Se flux to form a monolayer GaSe buffer on the substrate and to optimize surface smoothness. During the MBE growth process, SnSe₂ and its alloy phases form naturally when the Sn/Se flux ratio is less than 1:100. Sn₁₋ₓMnₓSe₂ samples with different Mn concentrations were obtained by using different Mn effusion cell temperatures. Each growth was preceded by deposition of a SnSe₂ buffer of a few nm, followed by the growth of the intended Sn₁₋ₓMnₓSe₂ of thicknesses between 40 to 70 nm, and capped by ~7 nm SnSe₂ and ~3 nm aluminum layers to prevent oxidation after the sample is exposed to the atmosphere.
Our interest in this paper is to examine the structural properties of the Sn$_{1-x}$Mn$_x$Se$_2$ layers as x increases in the alloy. X-ray diffraction (XRD) data obtained on these layers show sharp, well-resolved spectra characteristic of a single crystalline phase. The cross-sectional scanning transmission electron microscopy (STEM) images for a series of samples with increasing x were obtained using an FEI Titan 80-300 microscope, with STEM specimens prepared using an FEI-Helios focused ion beam (FIB) workstation. The energy dispersive X-ray (EDX) spectra were obtained using an FEI-Magellan 400 field-emission scanning electron microscope (FESEM) equipped with a Bruker energy dispersive X-ray spectrometer. In Figure 1 we show cross-sectional high-resolution TEM images for three layers with x = 0, 0.42 and 0.67, as determined by EDX. The TEM images are taken in the [110] direction of the GaAs substrate.

![SnSe$_2$, Sn$_{0.5}$Mn$_{0.42}$Se$_2$, Sn$_{0.33}$Mn$_{0.67}$Se$_2$](image)

**Figure 1.** HRTEM images and corresponding fast Fourier transform (FFT) data taken on Sn$_{1-x}$Mn$_x$Se$_2$ specimens with x = 0, 0.42 and 0.67 discussed in the text.

As seen in the figure, the Sn$_{1-x}$Mn$_x$Se$_2$ system retains the basic 2D character of the parent SnSe$_2$ material, but modified by an in-plane superstructure, as evidenced by the additional spots commensurate with the basic in-plane periodicity of this 2D structure. It is possible that, as Mn enters the SnSe$_2$ lattice, it tends to distribute itself not randomly, but in some periodically-ordered way. Work on detailed analysis of this structure is now in progress.

In conclusion, we feel that the accommodation of Mn magnetic ions in large concentrations in the SnSe$_2$-based 2D lattice, as shown by the results presented above, opens interesting new opportunities both for basic studies and for novel spintronic applications.

References:

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